Infrared spectra of the $Pd_nCO(n=2-5)$ molecules isolated in solid argon and neon between 100 and 4000 cm^{-1}

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- **Sorbonne Université (Université Pierre et Marie Curie), Paris, France**
- **Laboratoire MONARIS:** de la **Mo**lécule aux **Na**no-objets :

Réactivité, **I**nteractions et **S**pectroscopies

THE Pd_nCO MOLECULES

- Important role played by the CO in transition metal complexes
- Model compounds to study the CO-palladium bond

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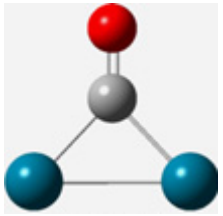

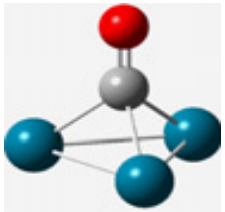

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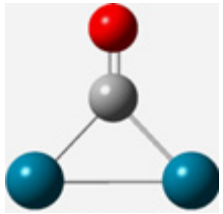

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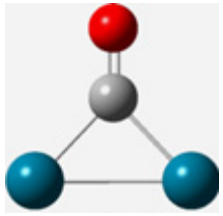

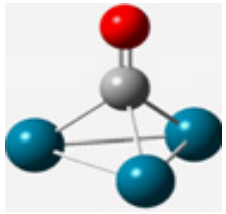

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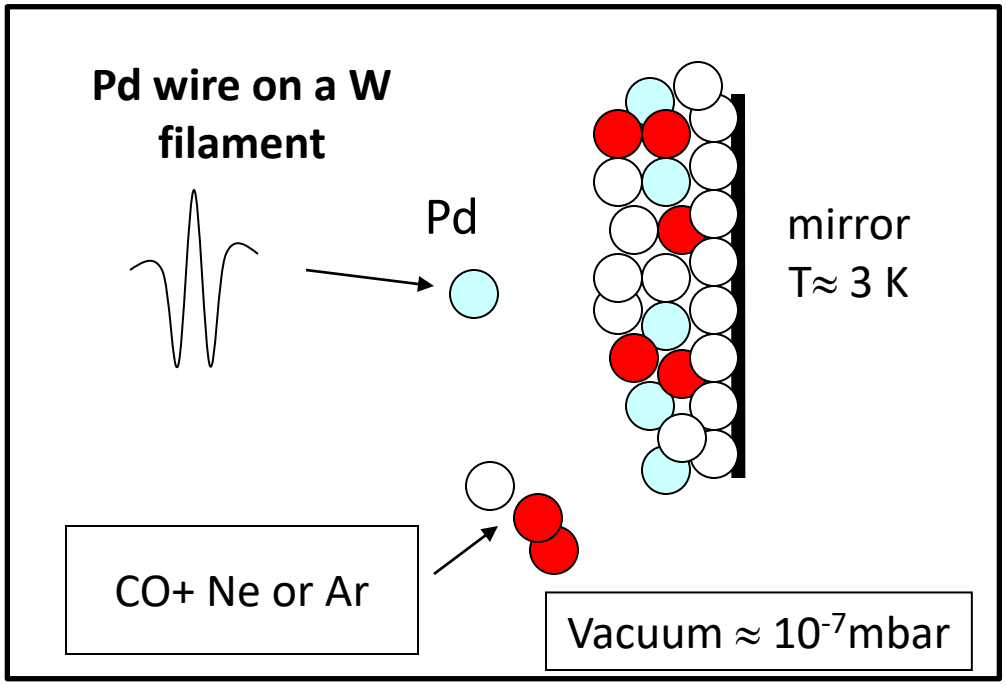
- Matrix isolation is used to stabilize small metal molecules in quantities large enough to enable detection in the mid and far infrared
- Possibility to observe the low intensity bands

SAMPLE DEPOSITION



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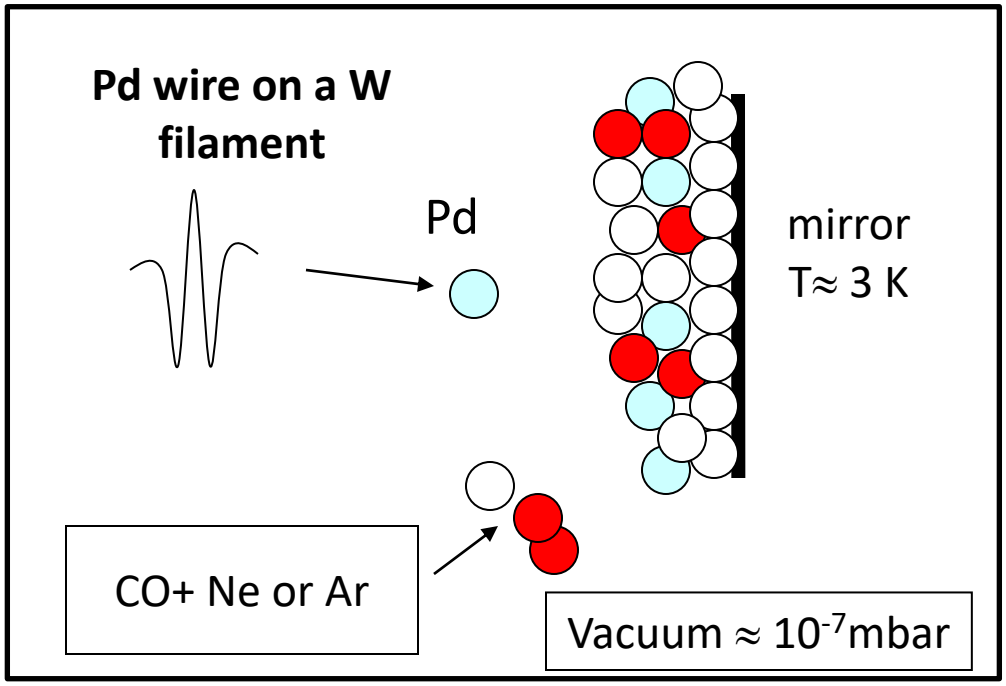

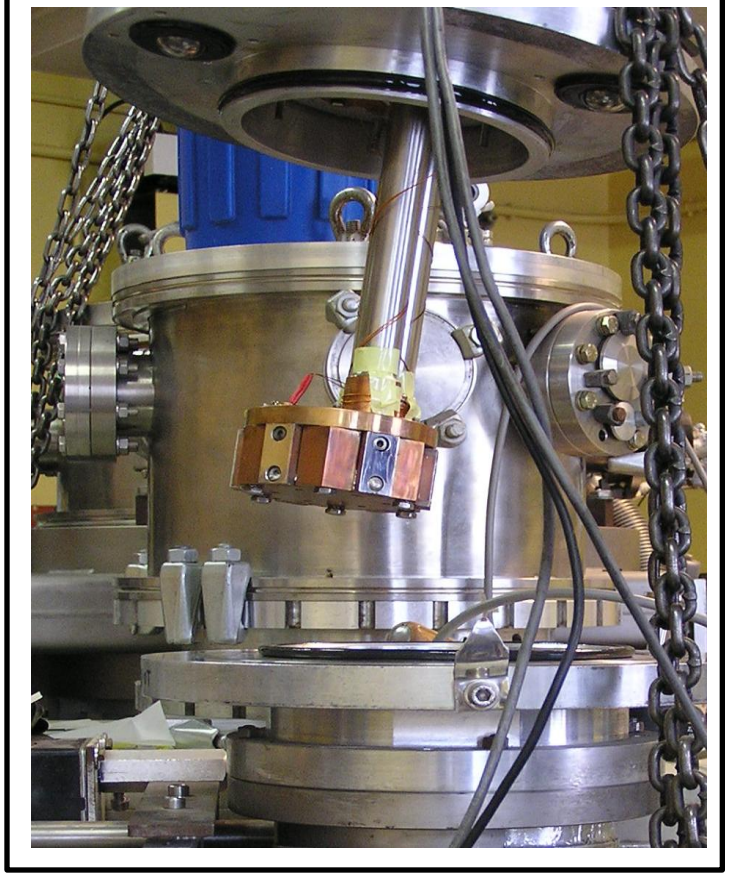

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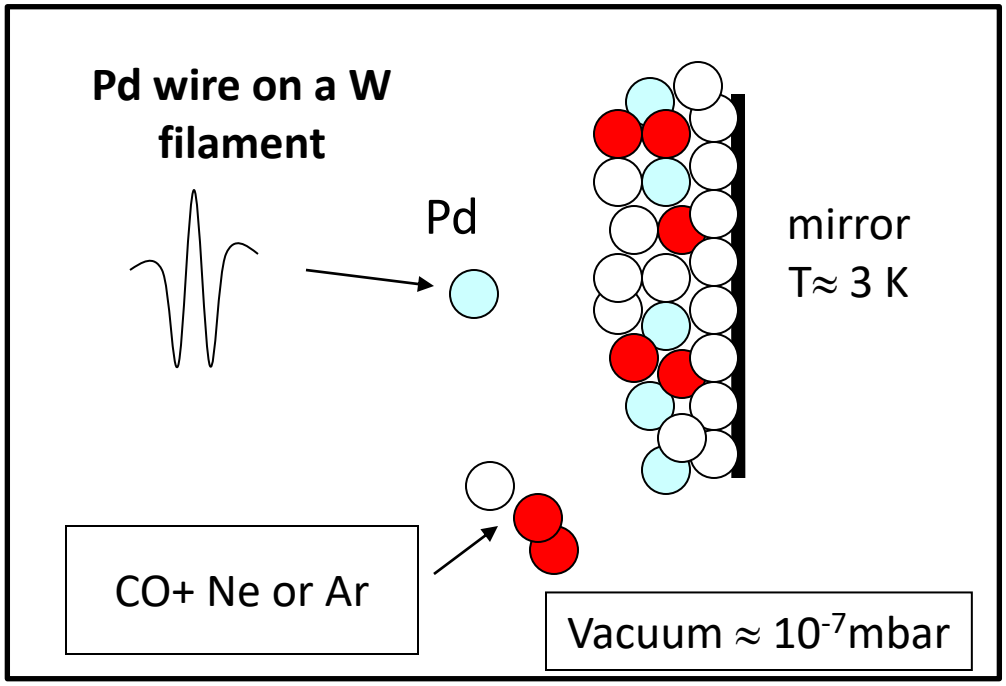

- Thermal evaporation: the metal atoms are in the ground state

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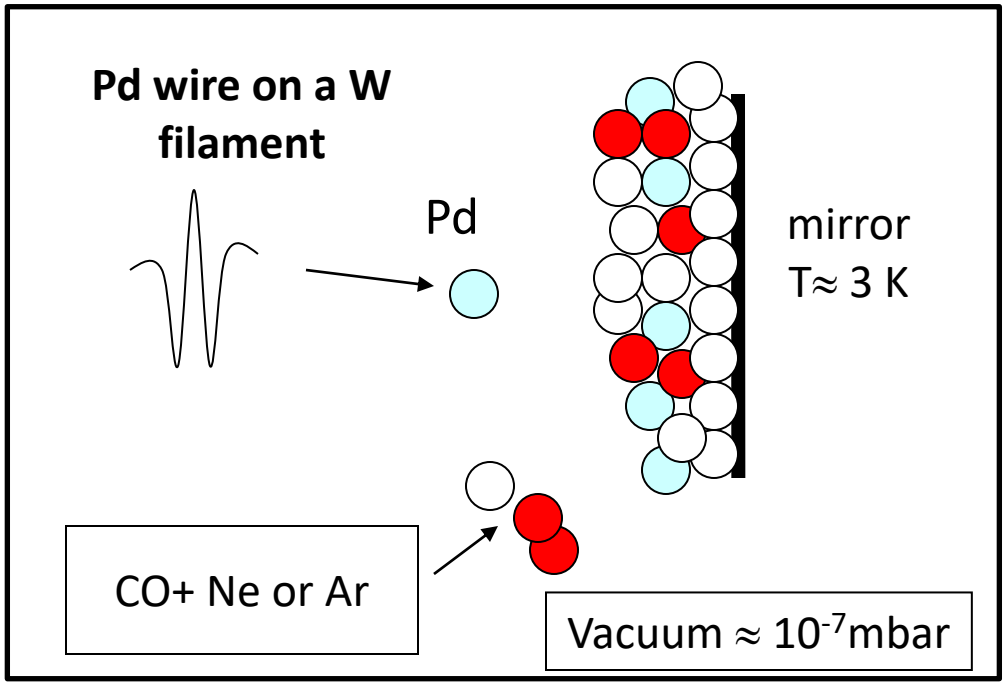
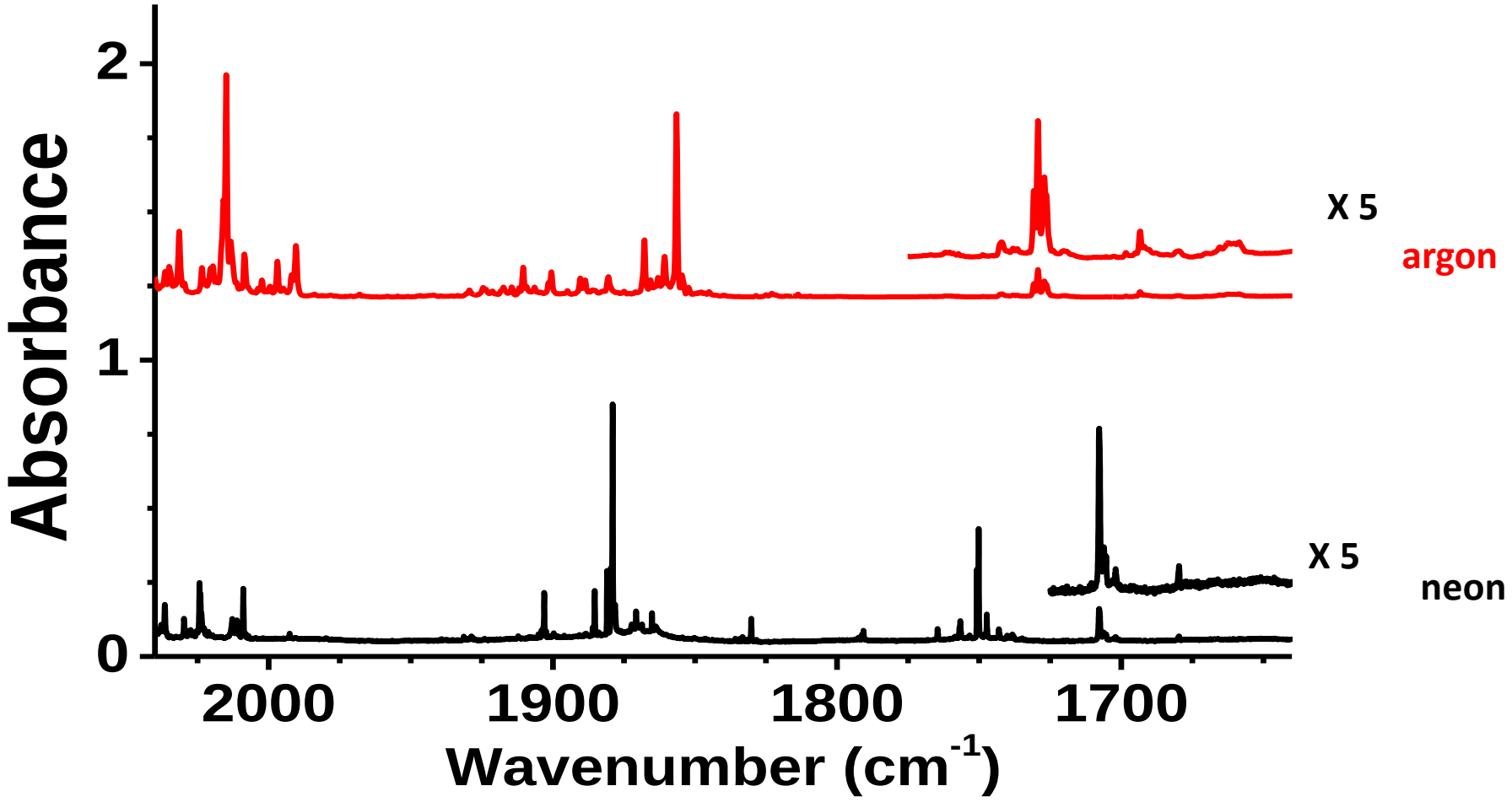


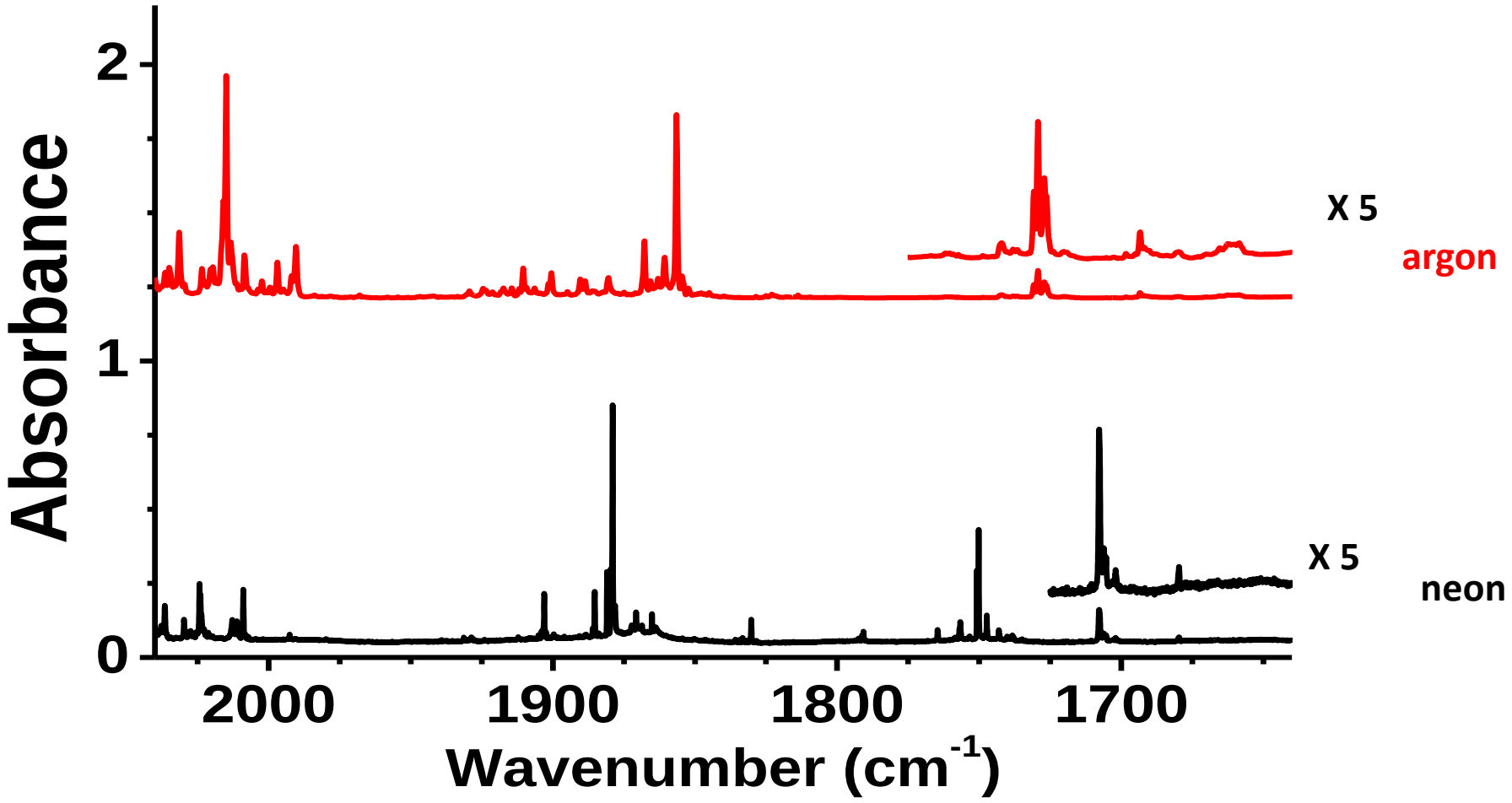
- absorption spectra in the near-, mid- and far infrared were collected on the same sample, with a Bruker 120 FTIR spectrometer and InSb or MCT or bolometer detectors.

New bands in the CO stretching region



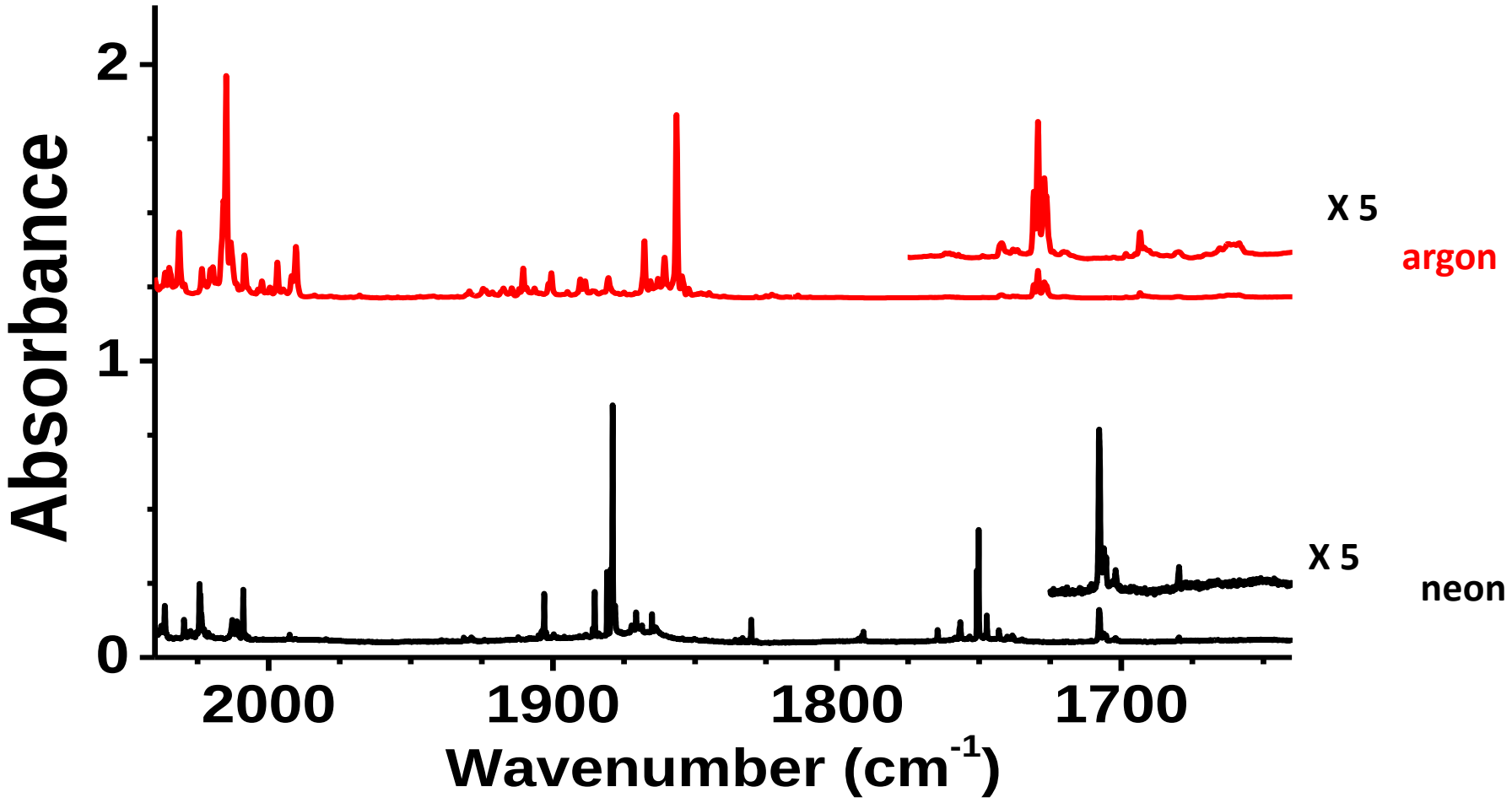
New bands in the CO stretching region

$Pd_n(CO)_m$ → n:m molecules



New bands in the CO stretching region

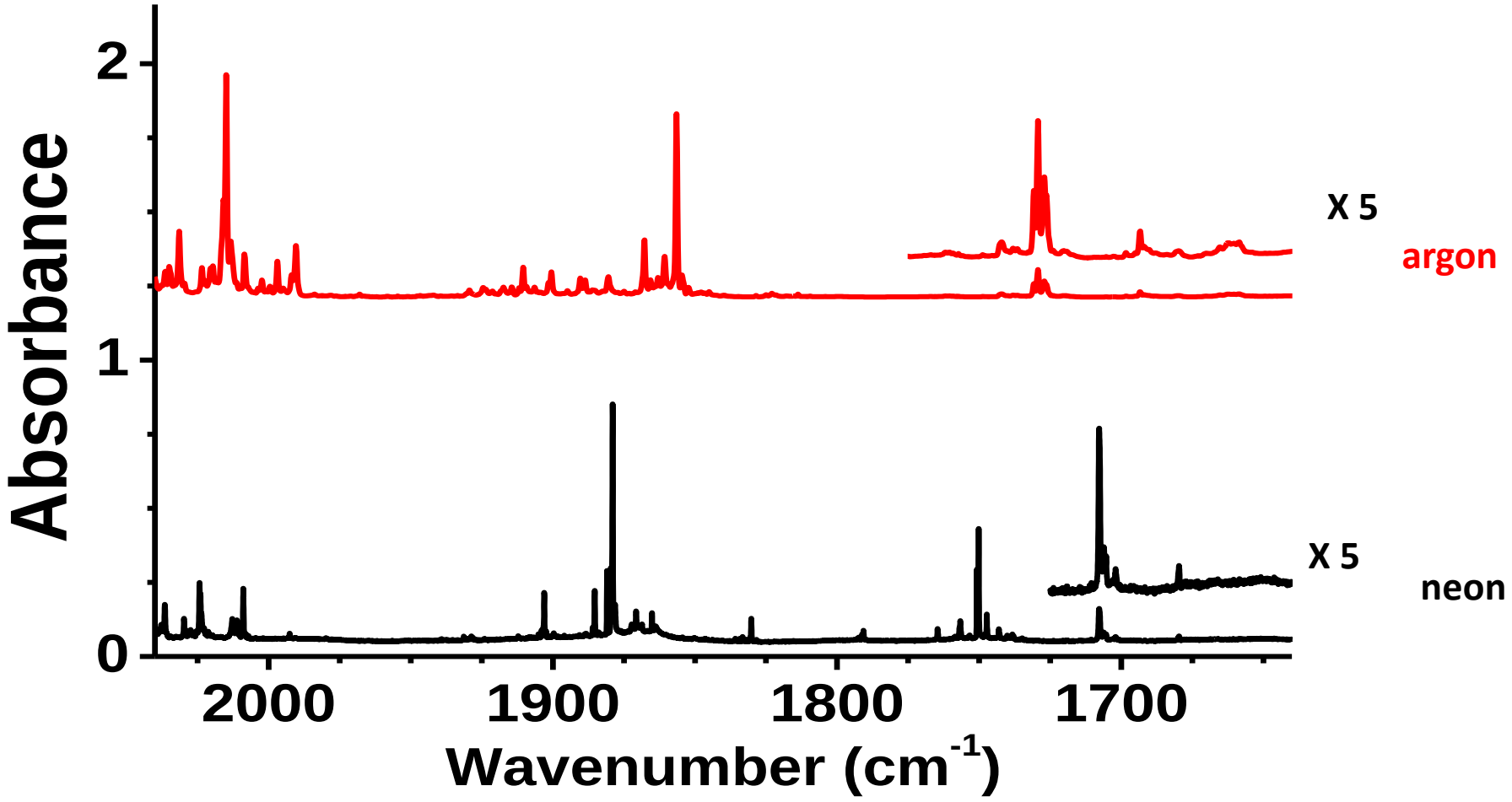
Between 2040 and 2080 cm^{-1}: 1: m molecules



New bands in the CO stretching region

-In argon and neon : concentrations were varied over a large range

- Ne : easier atomic diffusion ➡ higher formation of n: 1 with n > 2



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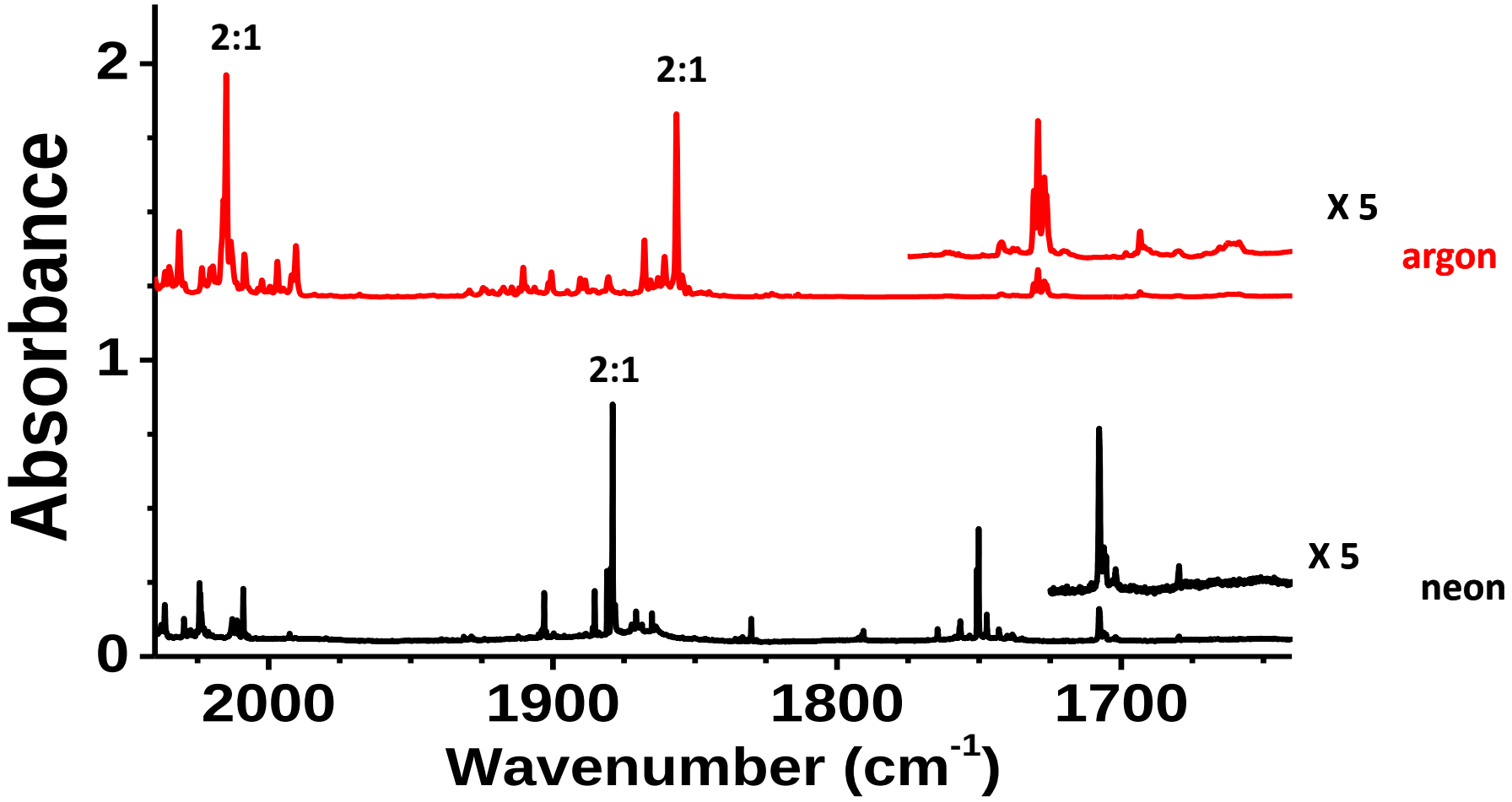

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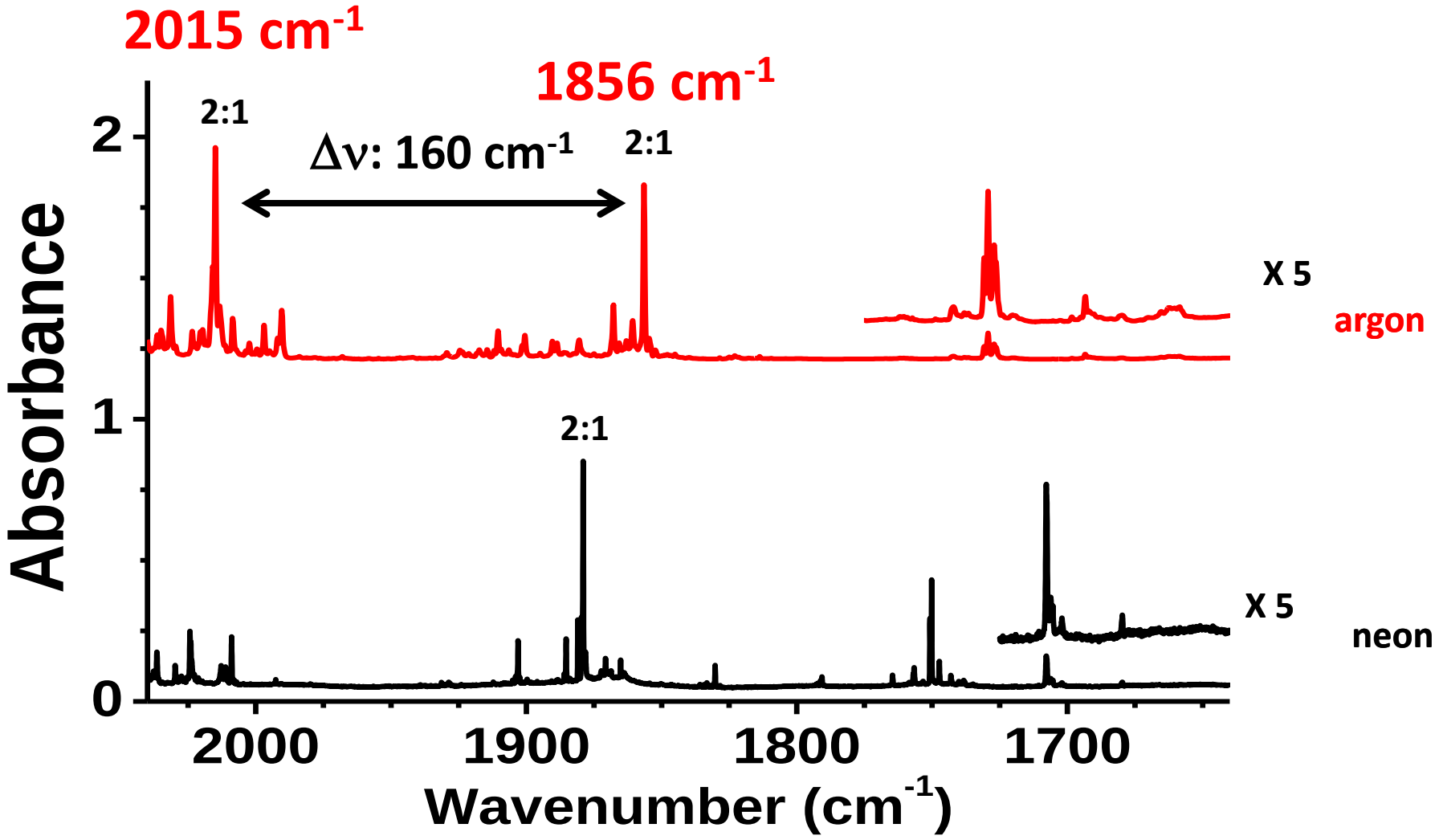

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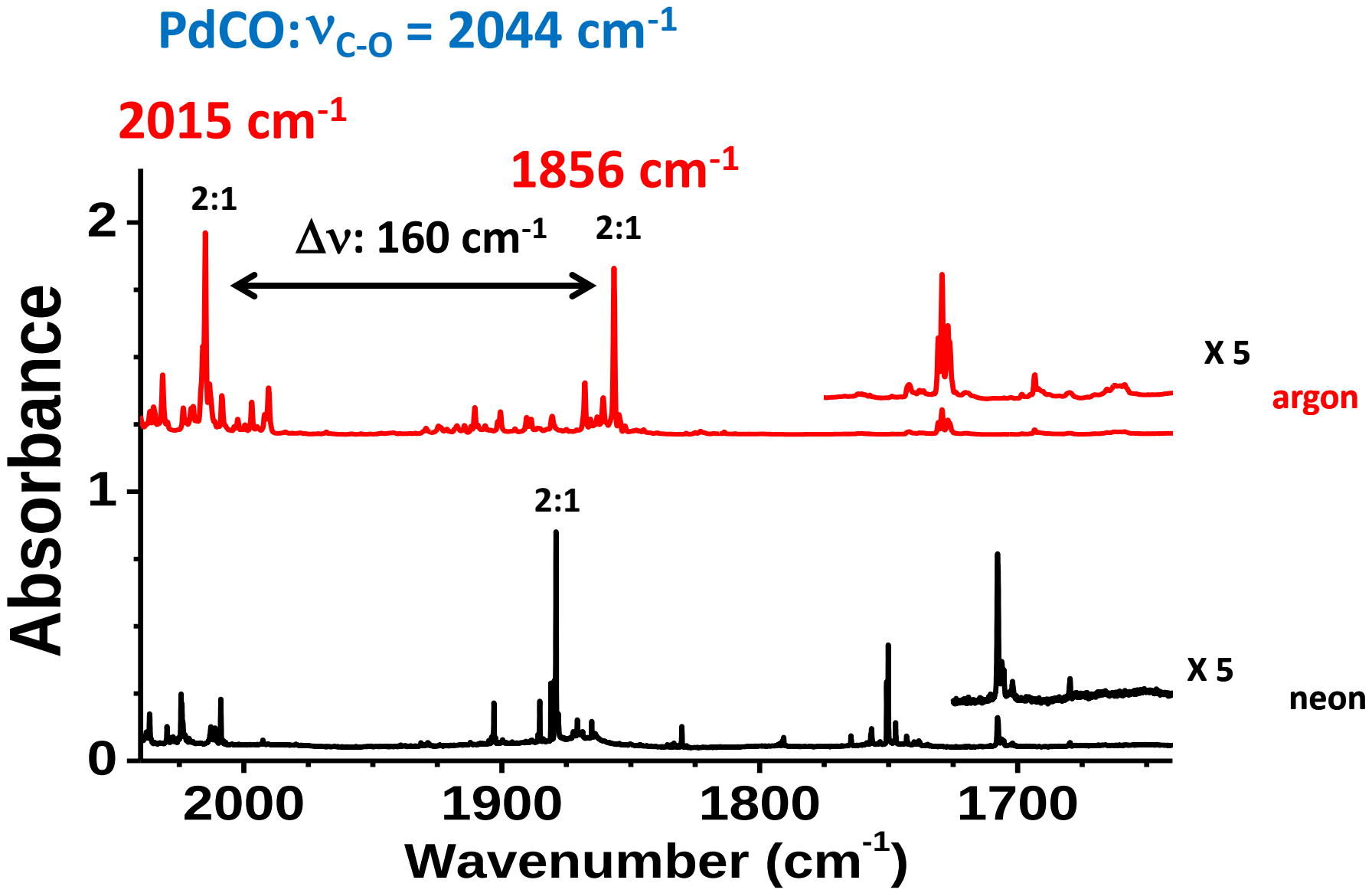

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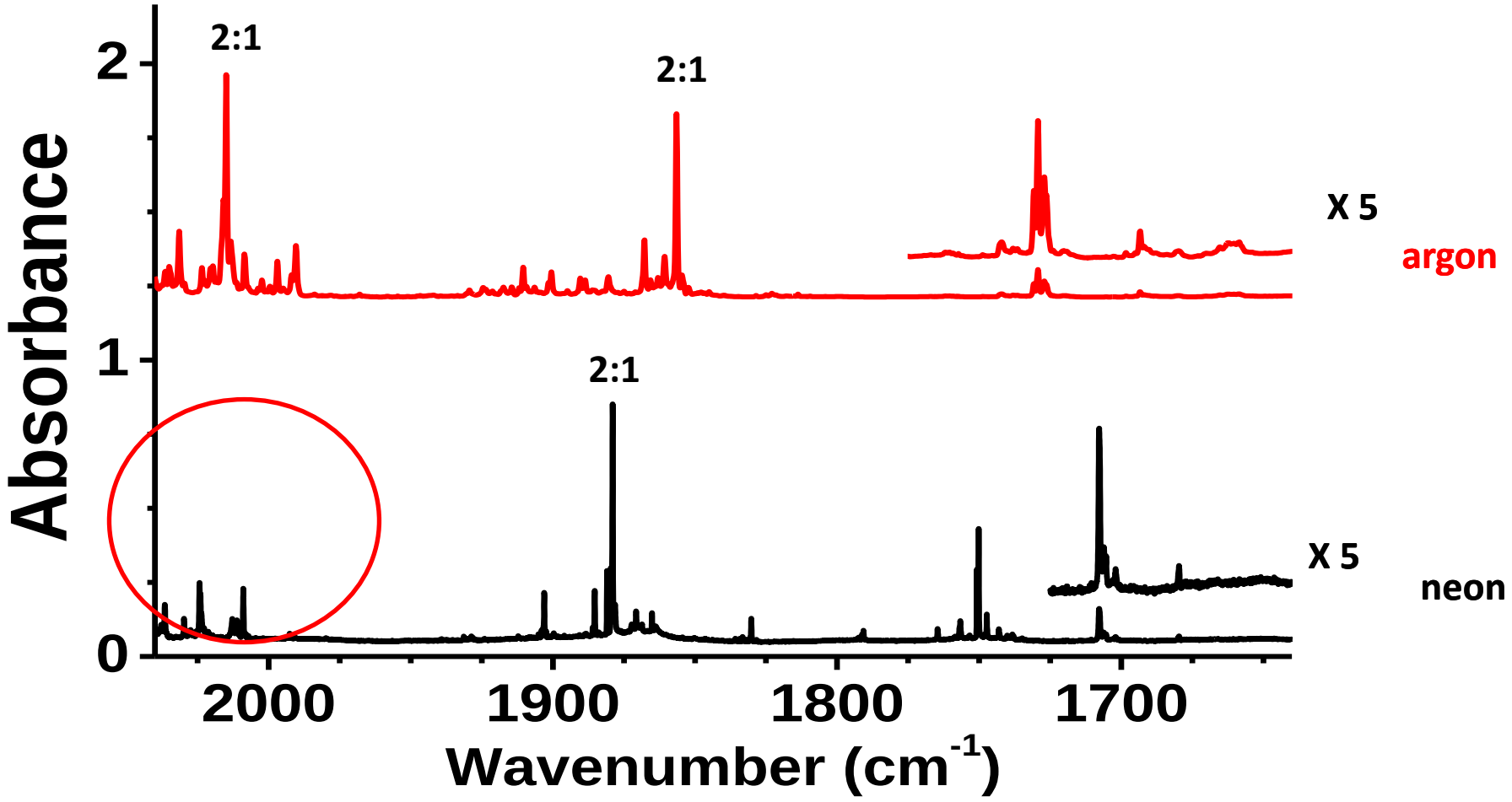

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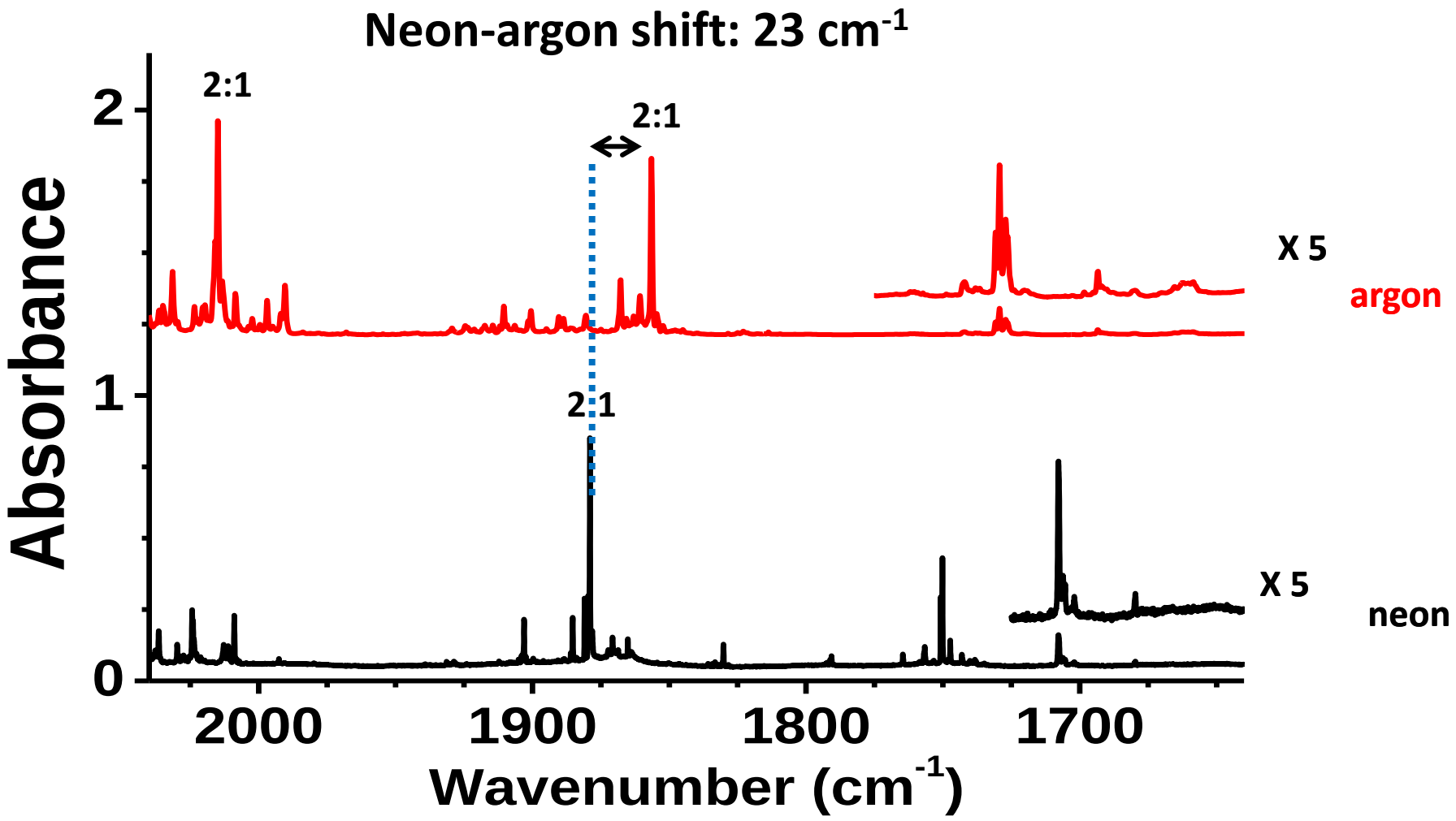

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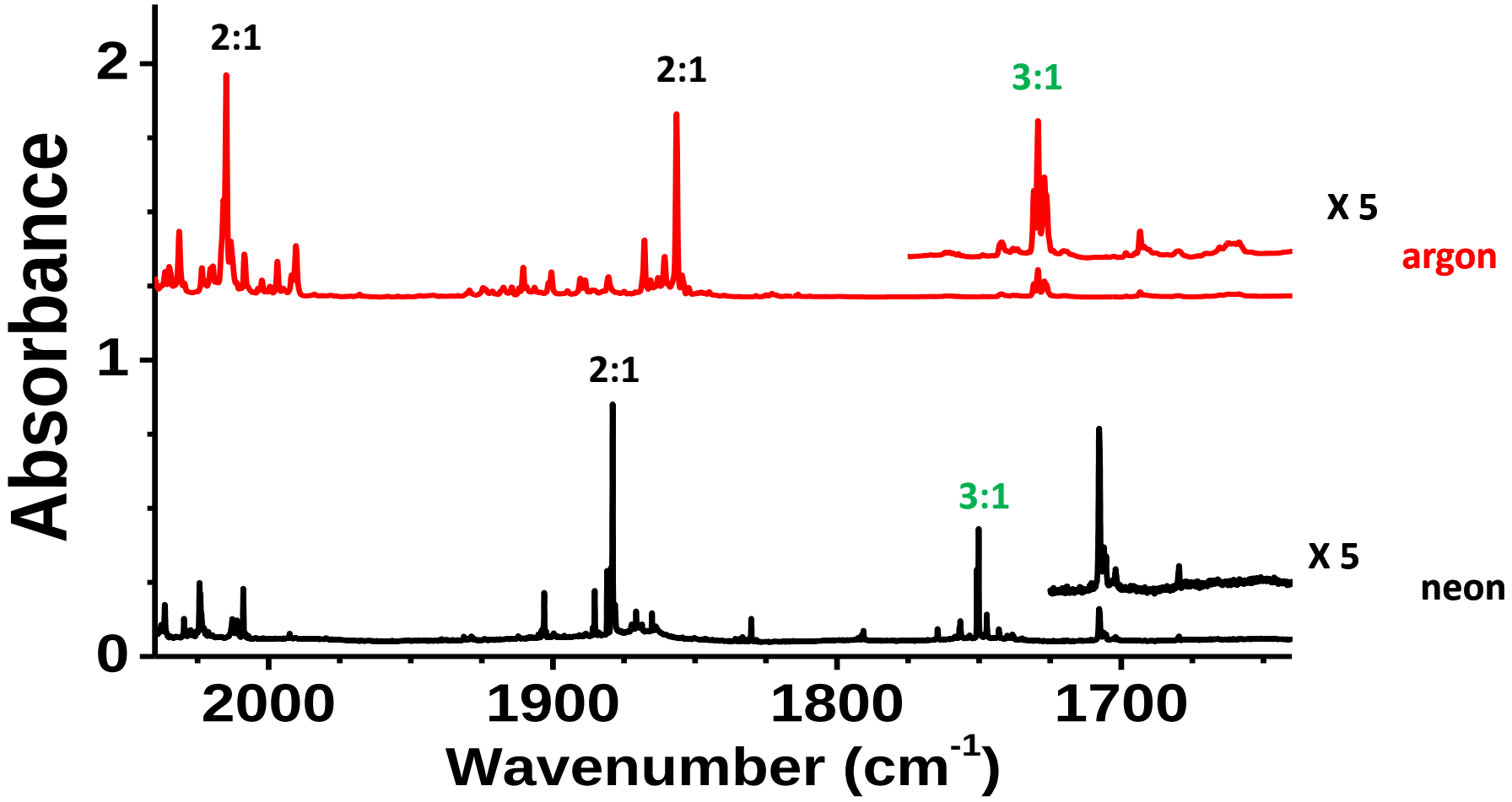

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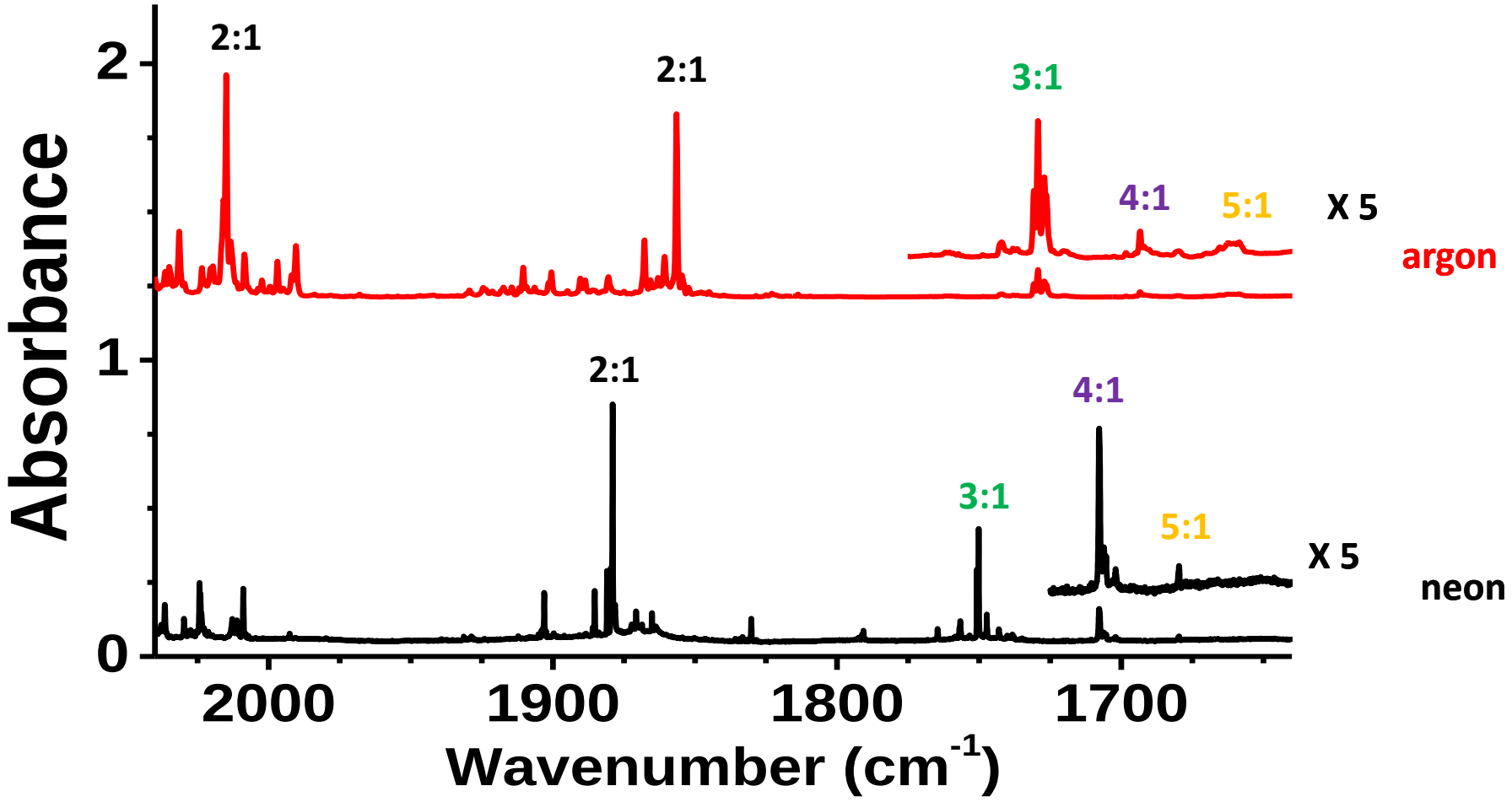

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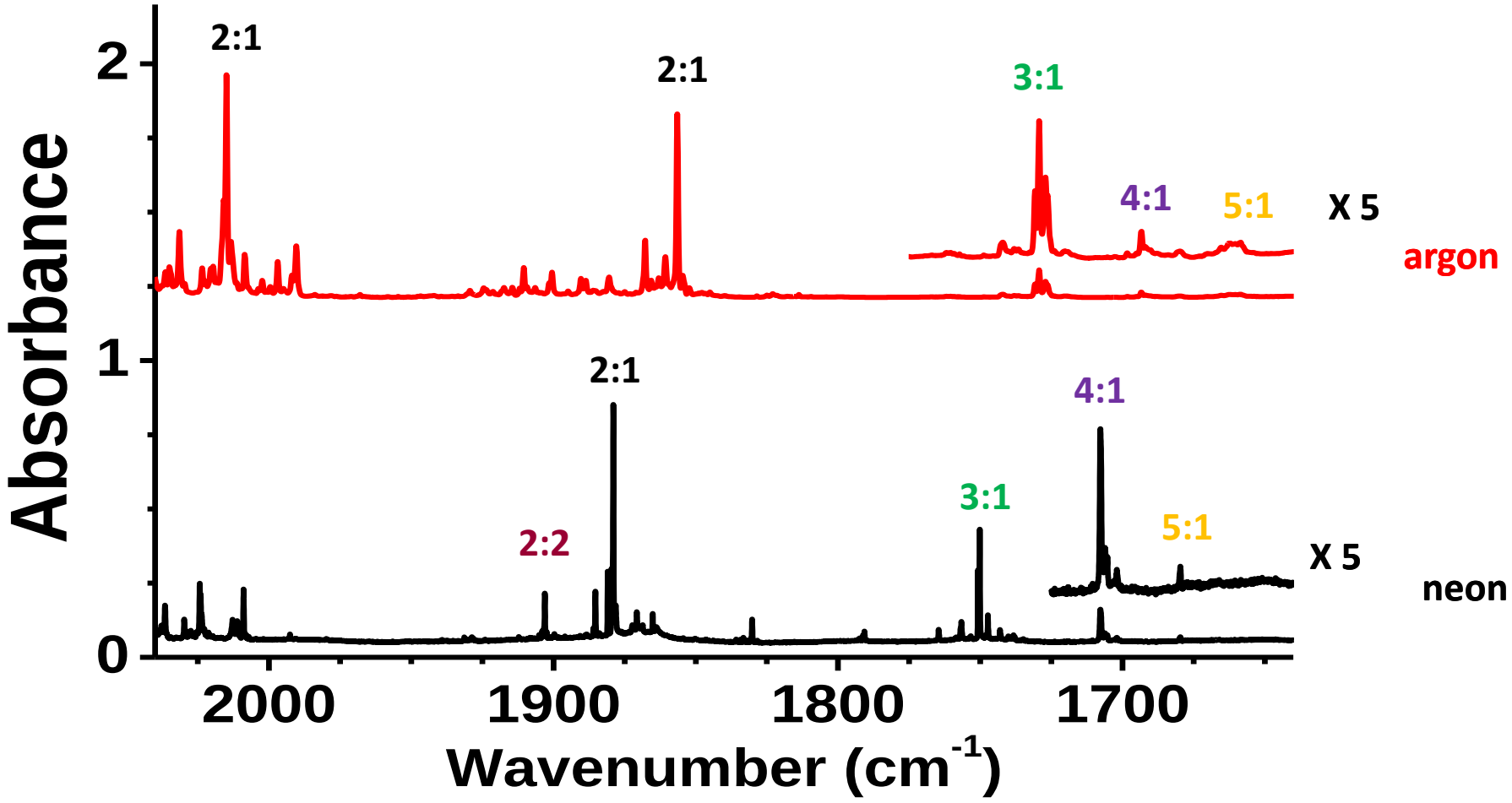
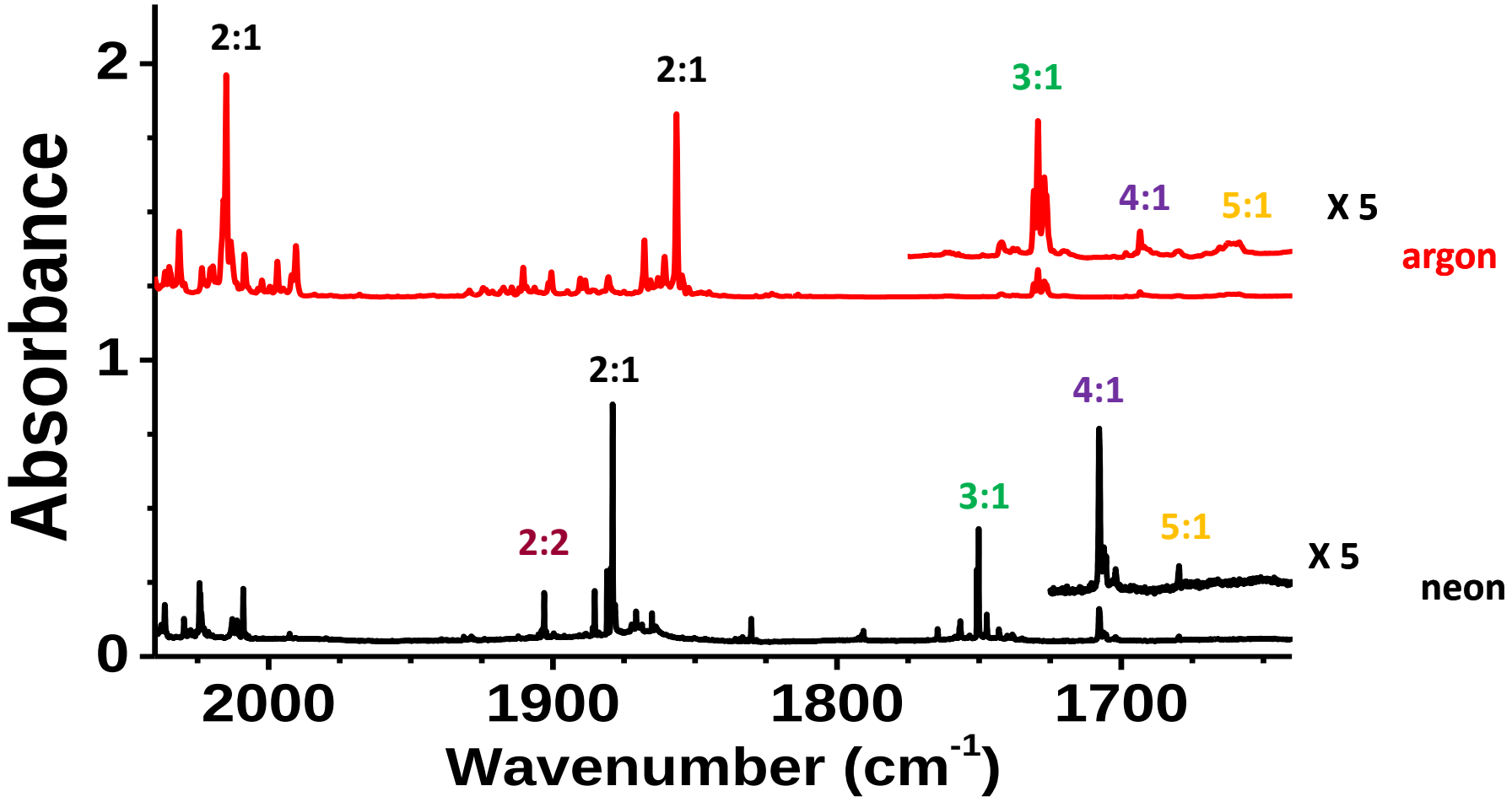
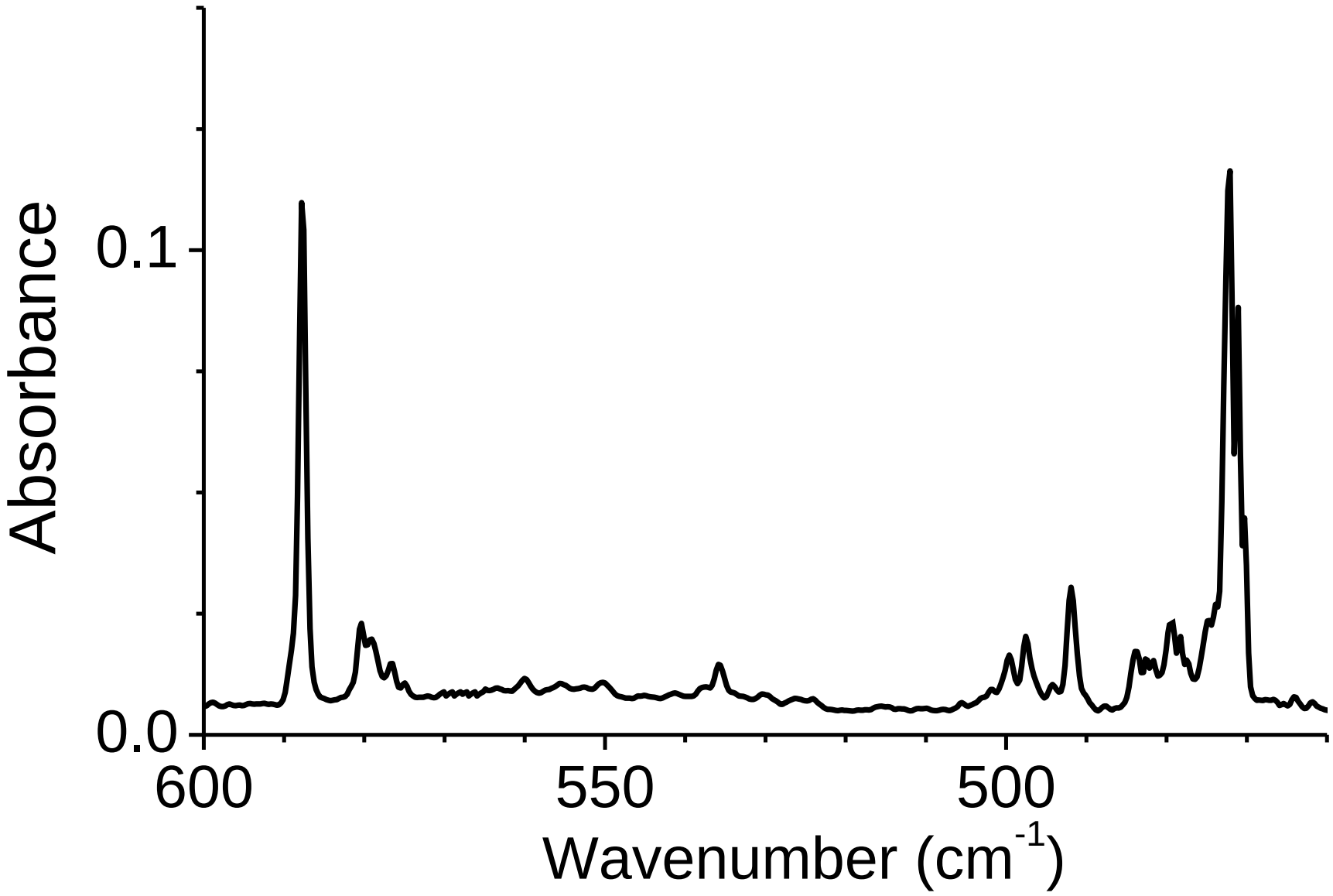


New bands in the CO stretching region

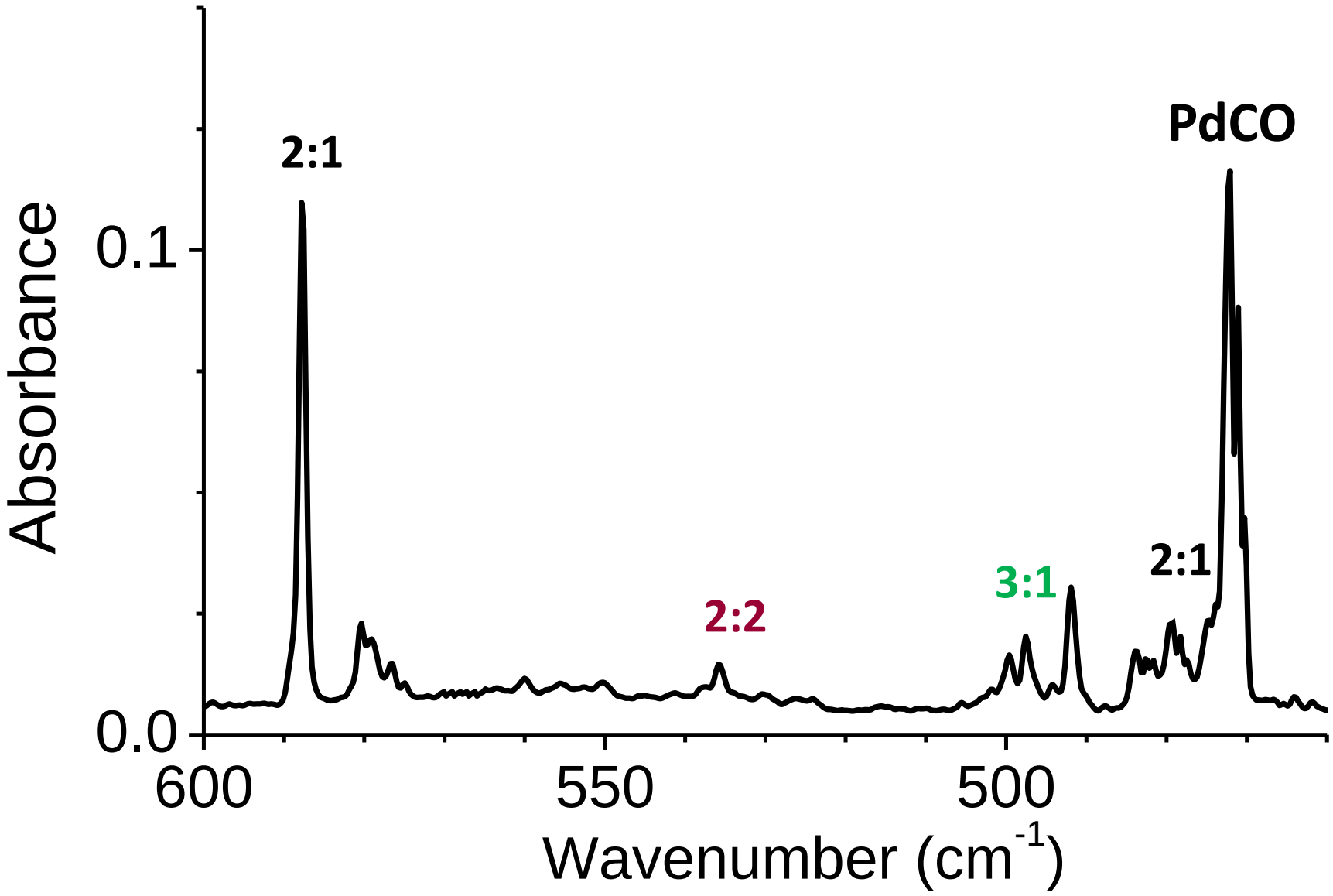
all the bands were observed with $^{13}C^{16}O$ and $^{12}C^{18}O$ isotopes



New bands in the far infrared region



New bands in the far infrared region: argon



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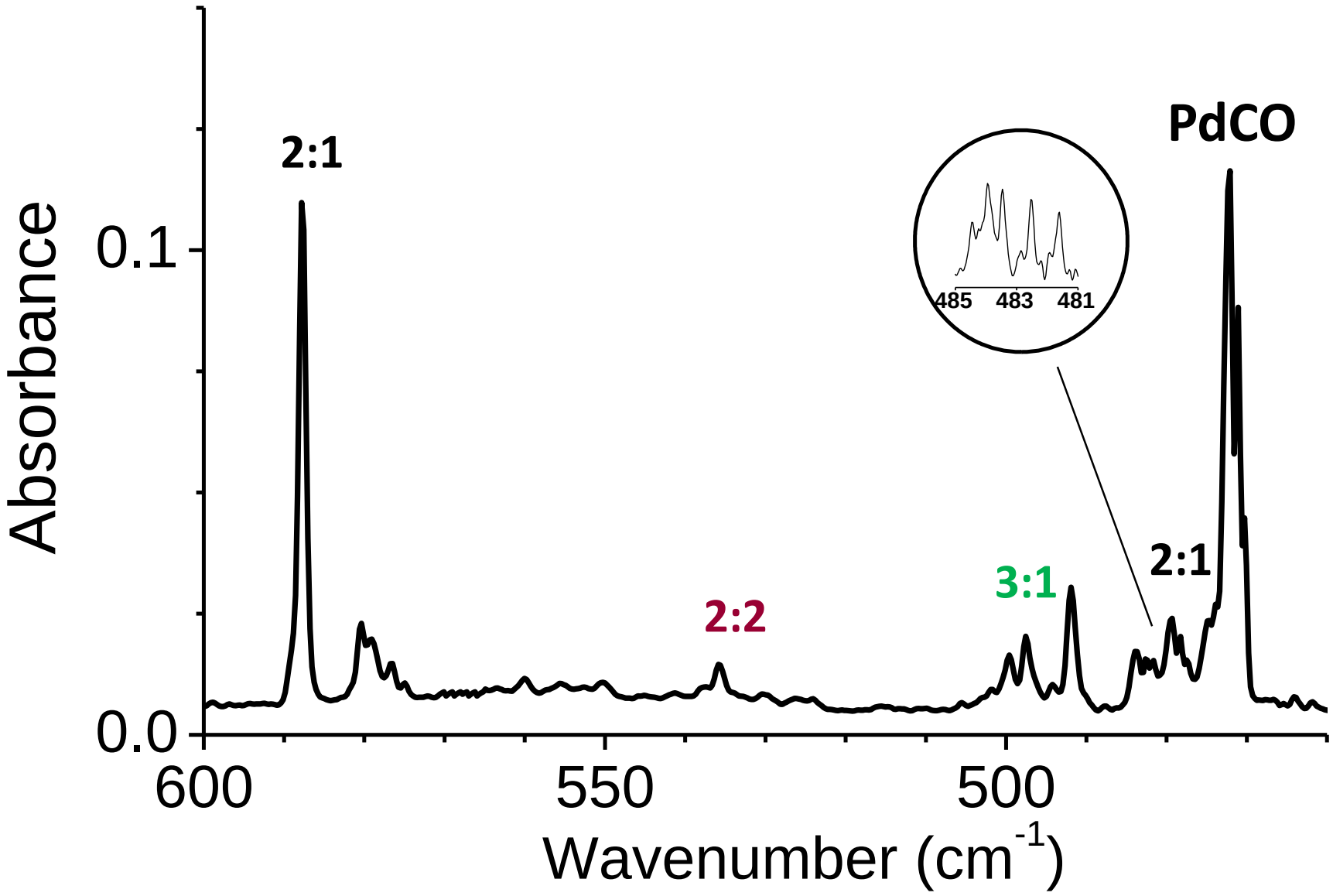

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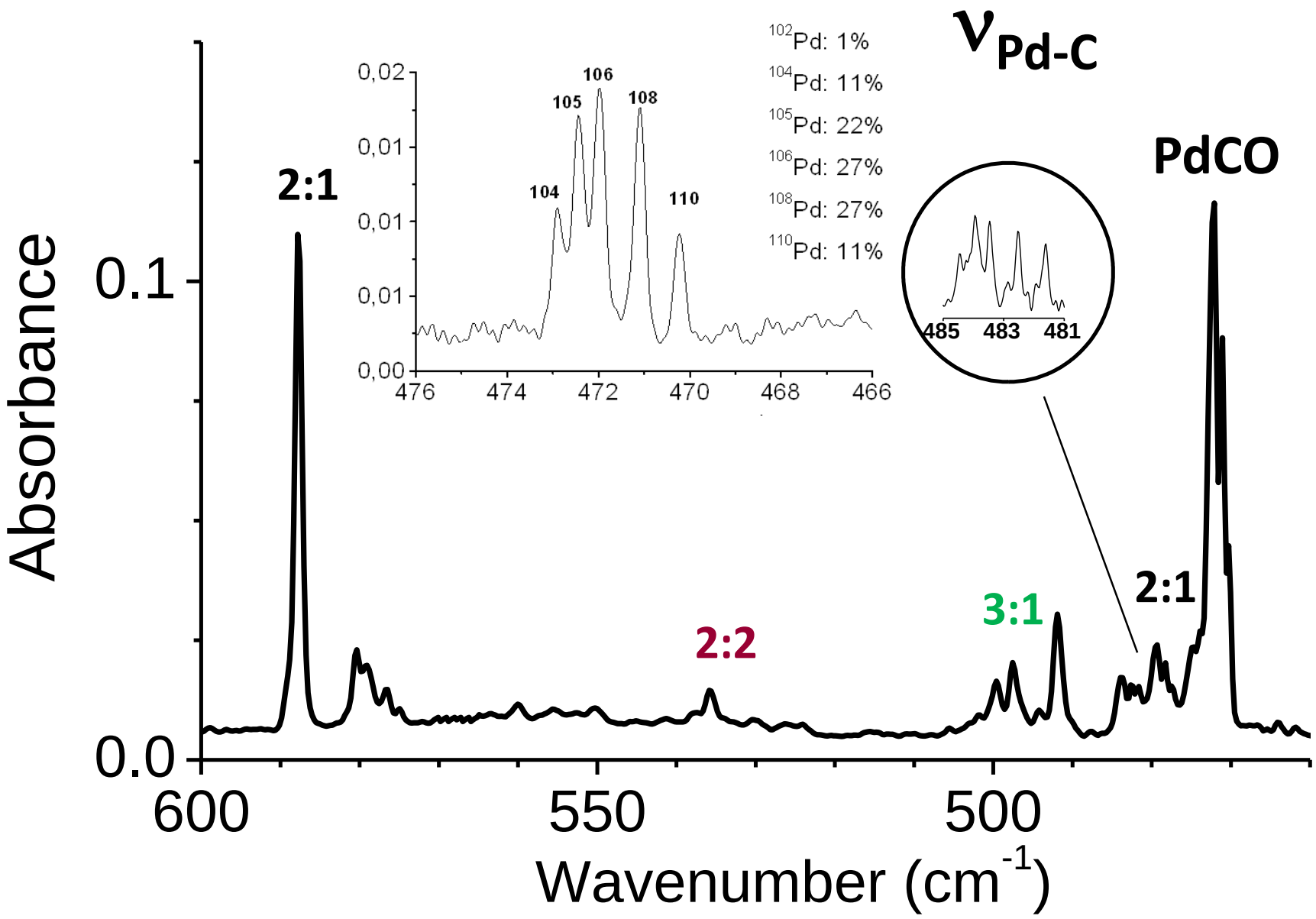

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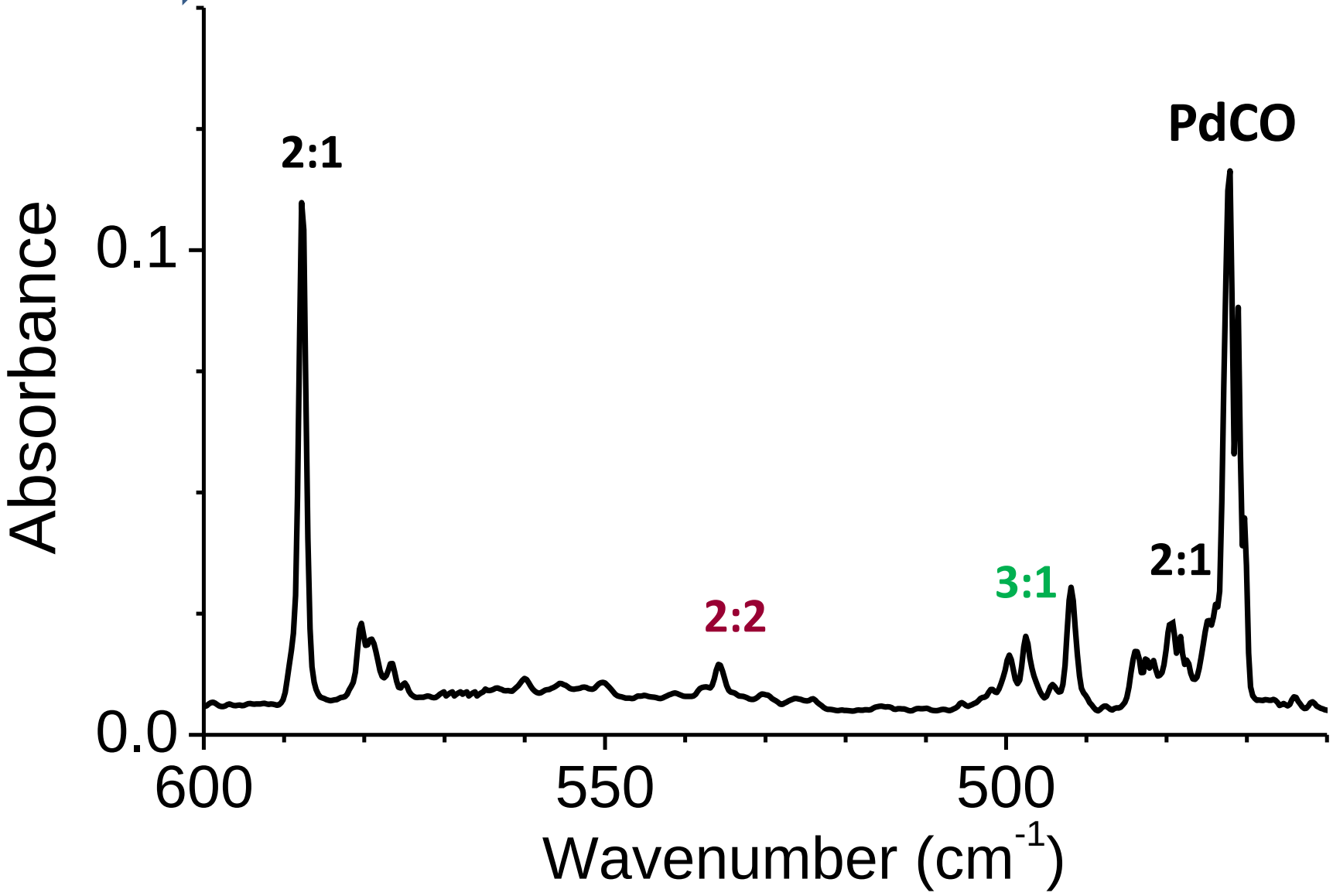

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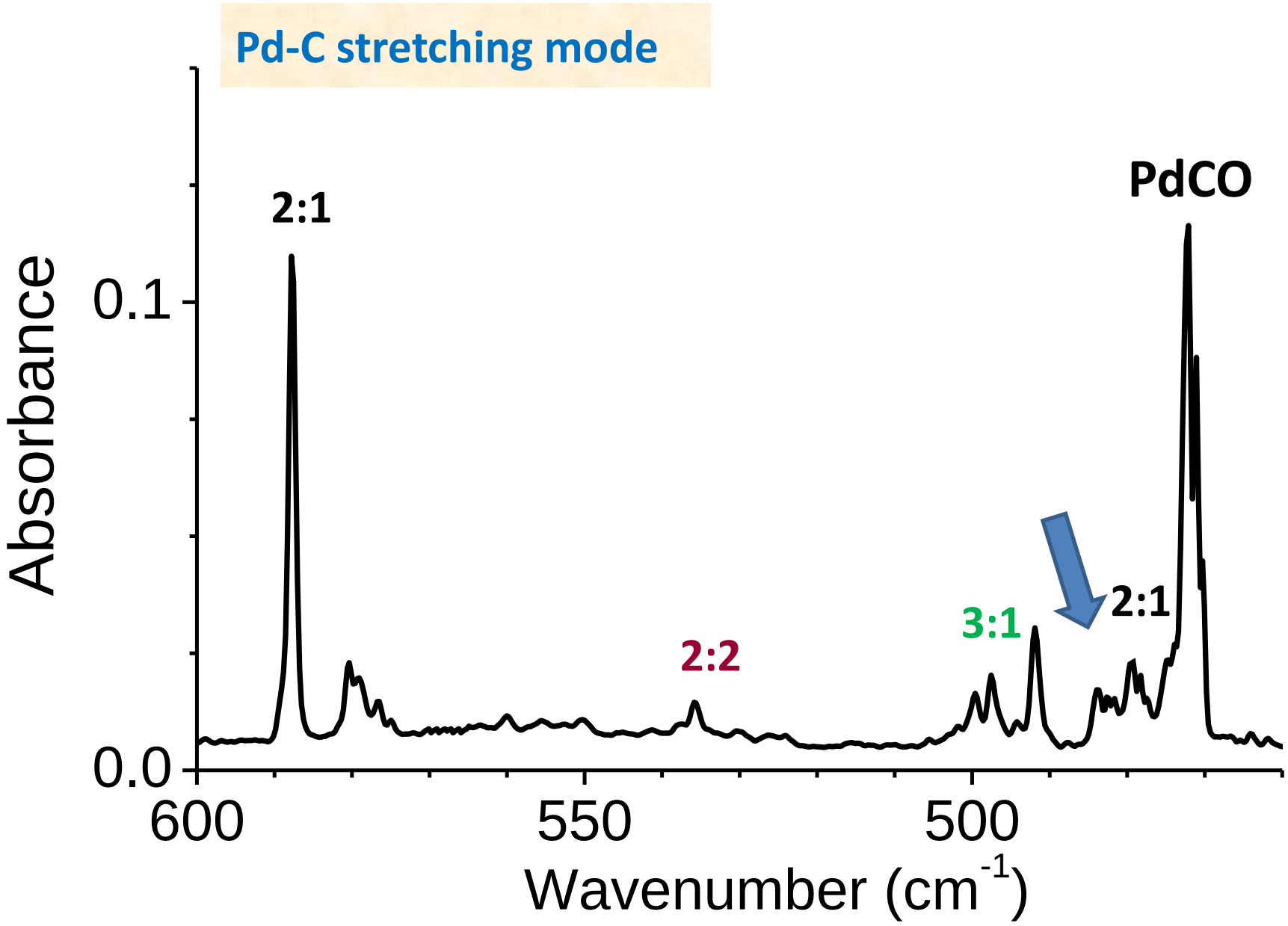
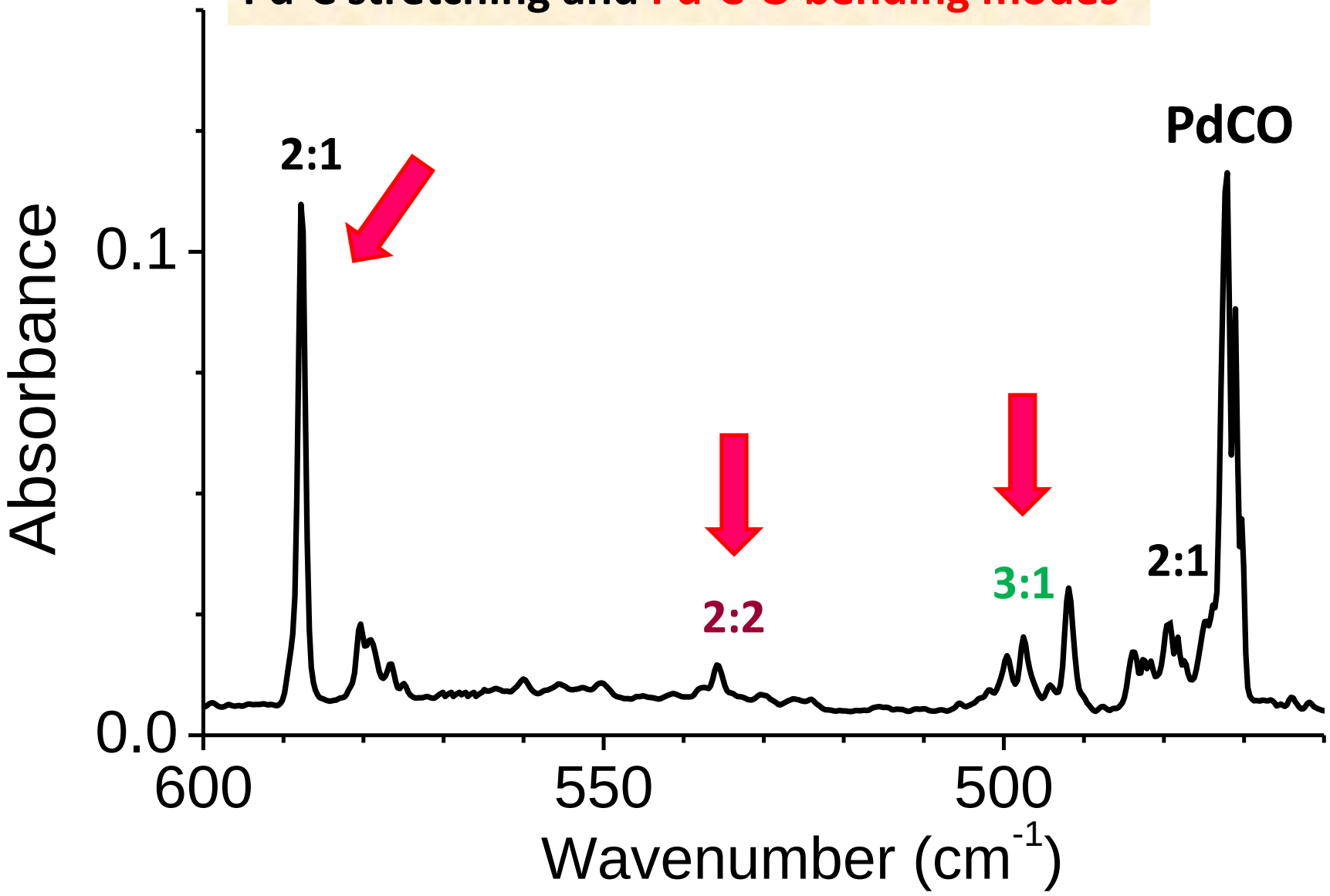
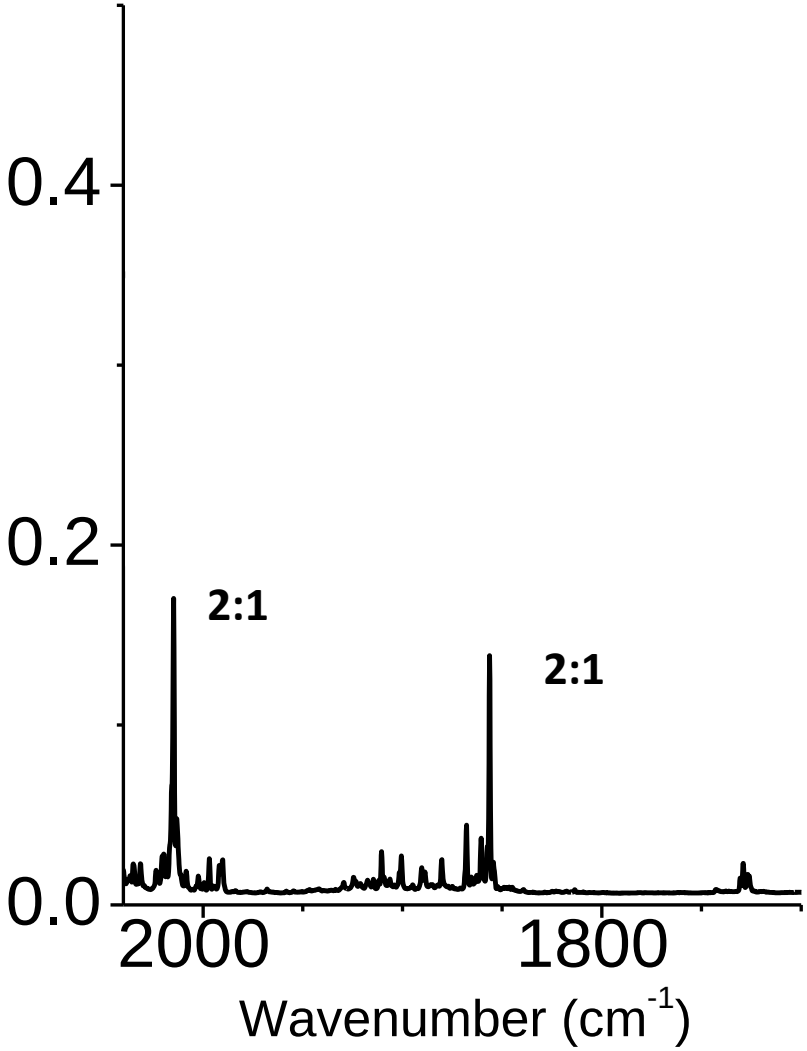


New bands in the far infrared region: argon

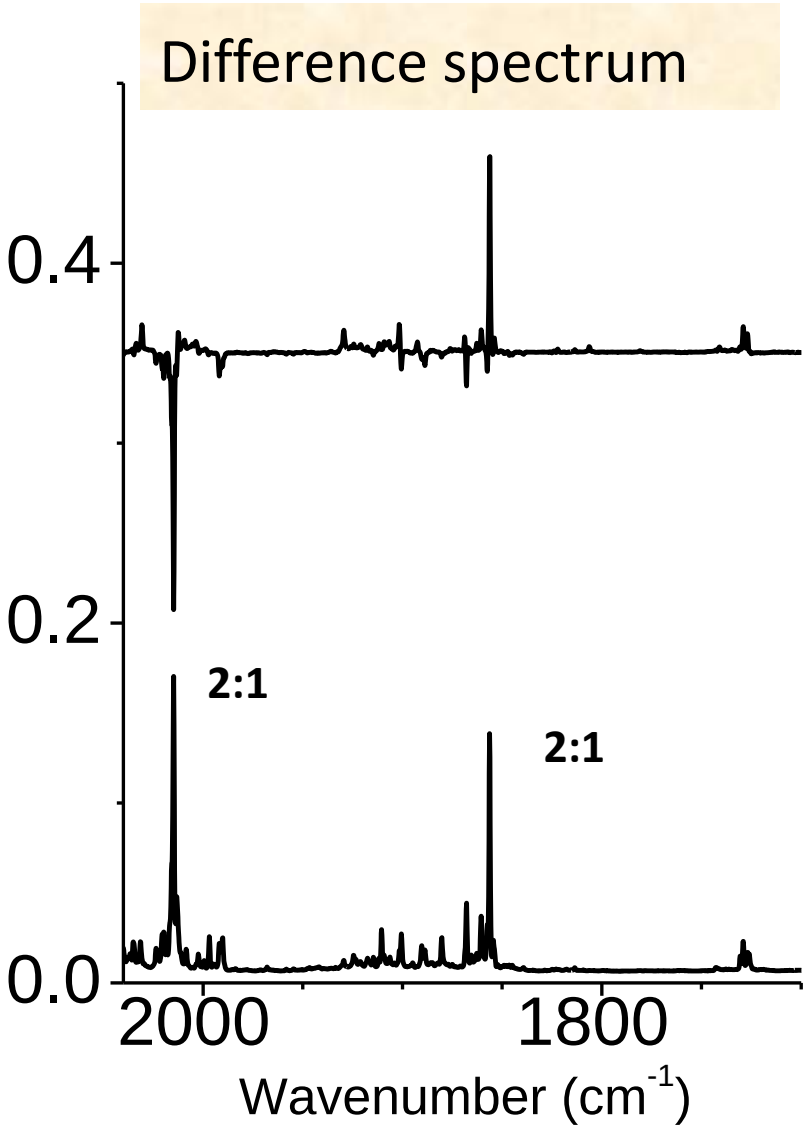
Pd-C stretching and Pd-C-O bending modes



Why two bands for the 2:1 molecule?



Photolysis: Irradiation at λ = 405 nm



No data on the electronic spectra of Pd_n

Only on atomic Pd

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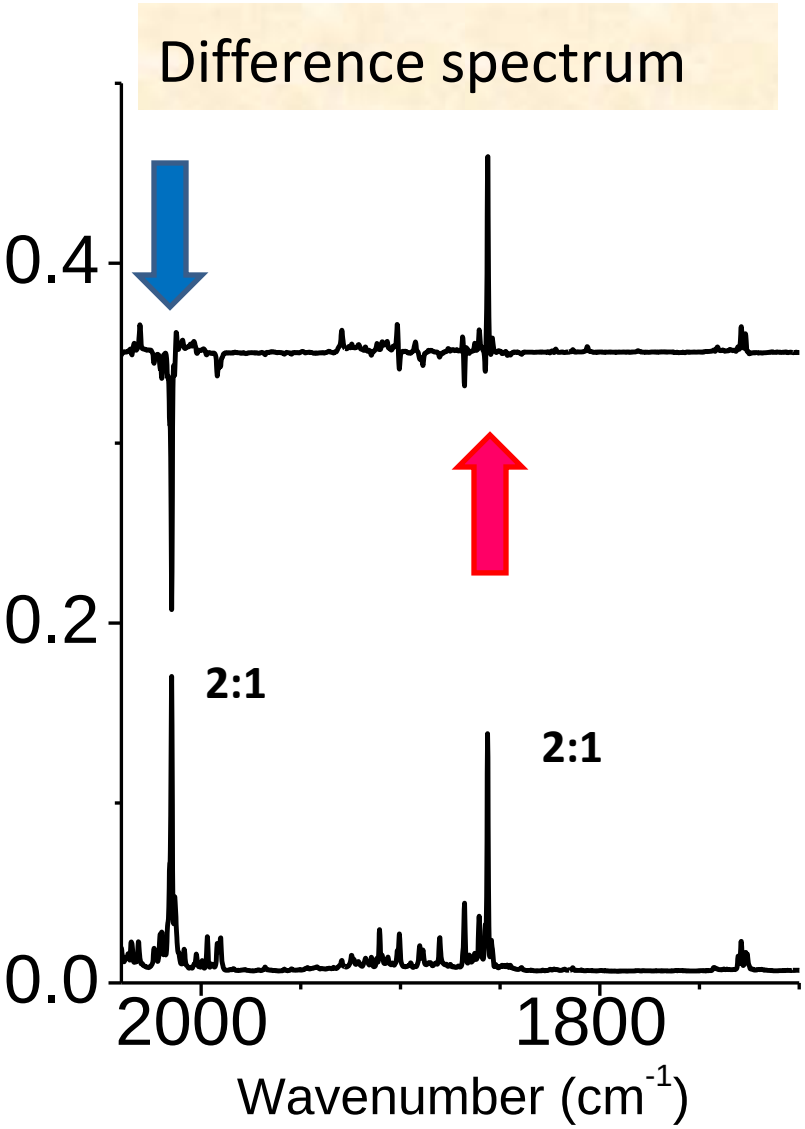

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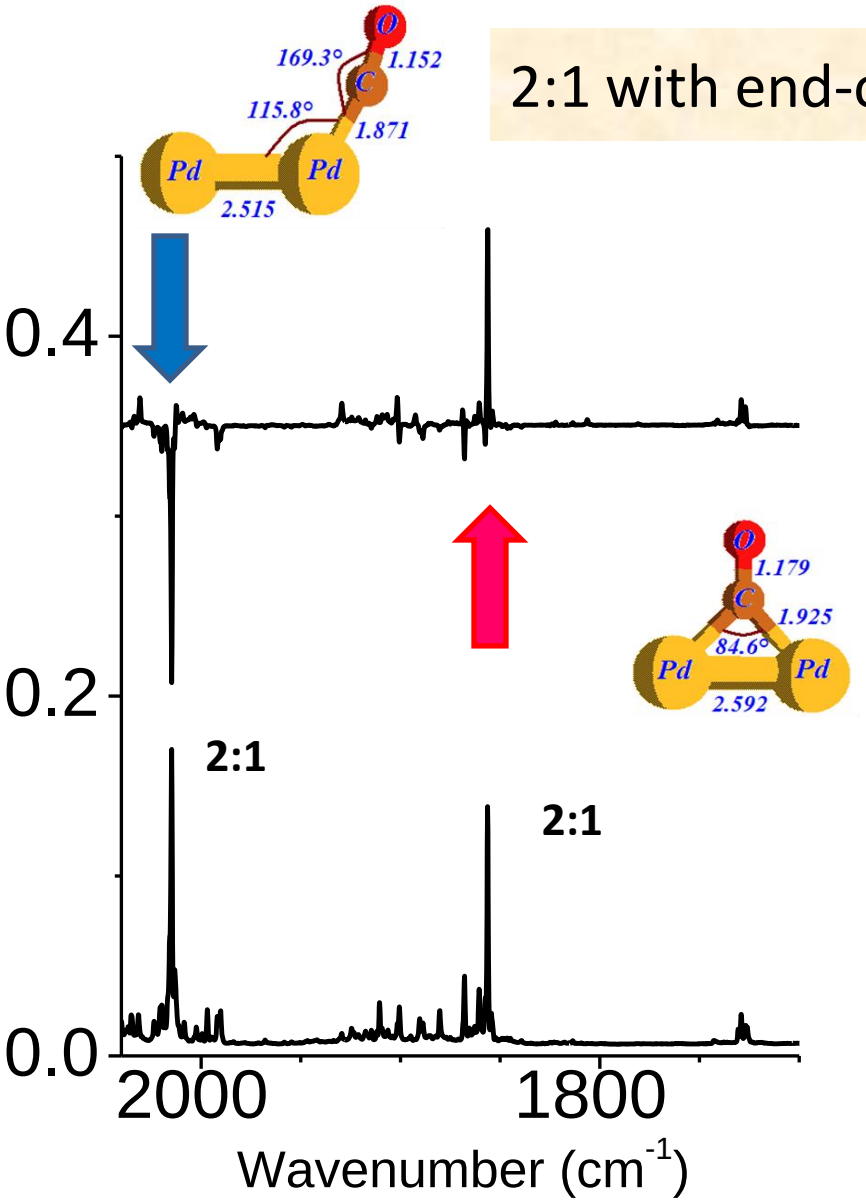

2:1 with end-on structure

2:1 with bridged structure

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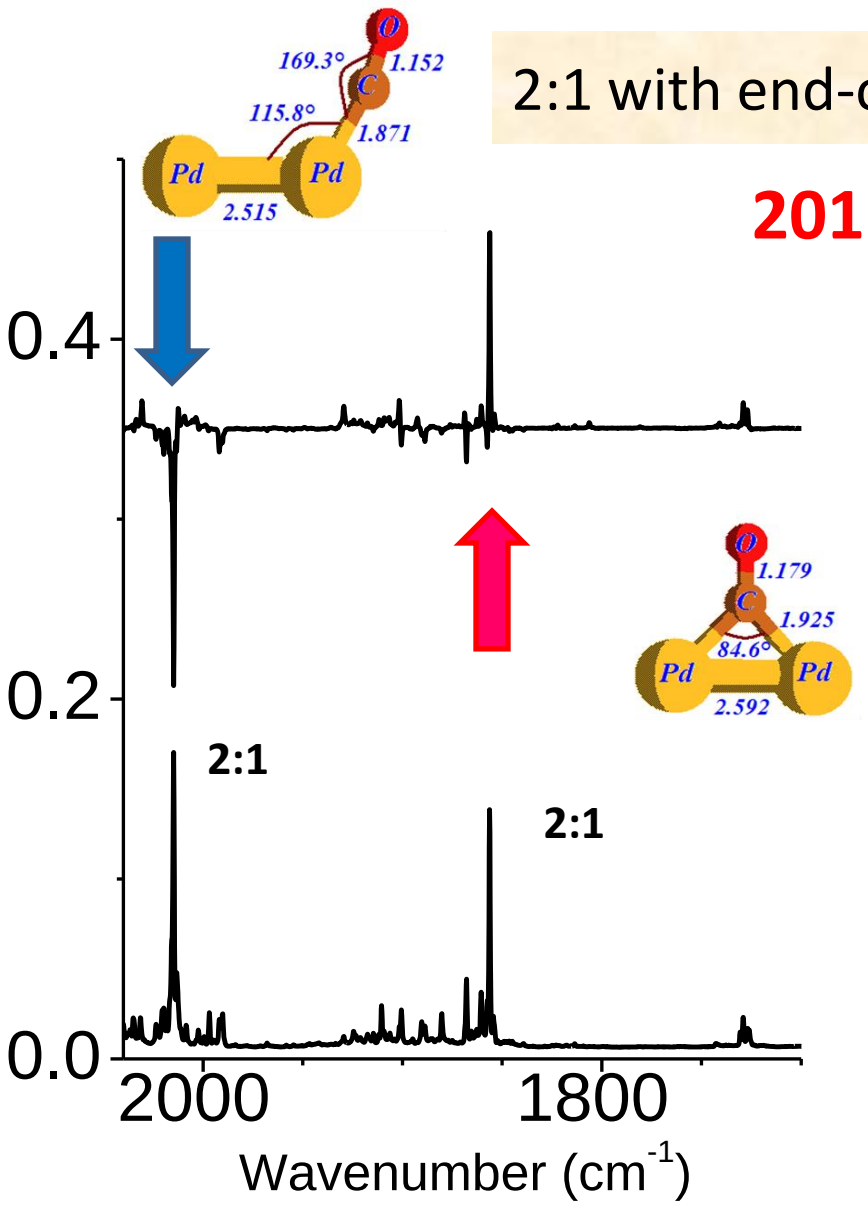

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2015 cm^{-1}

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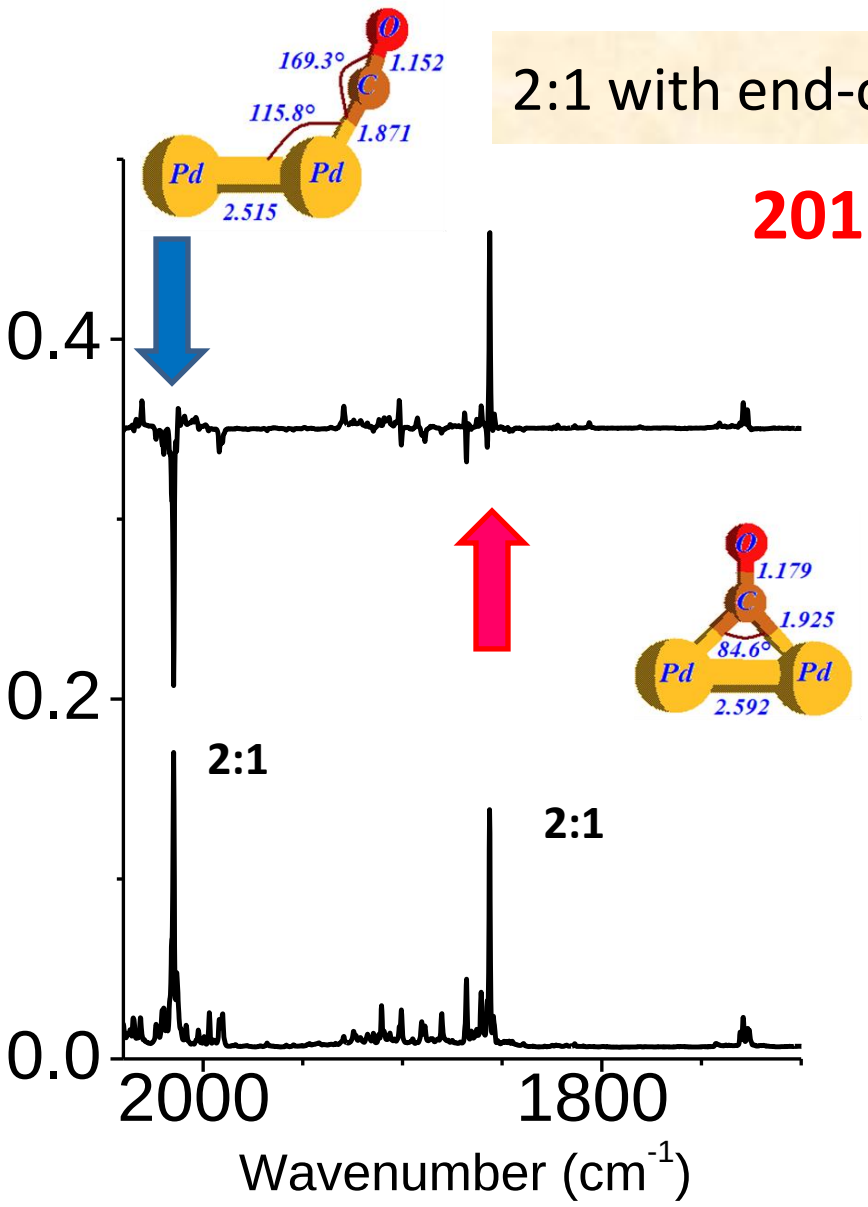

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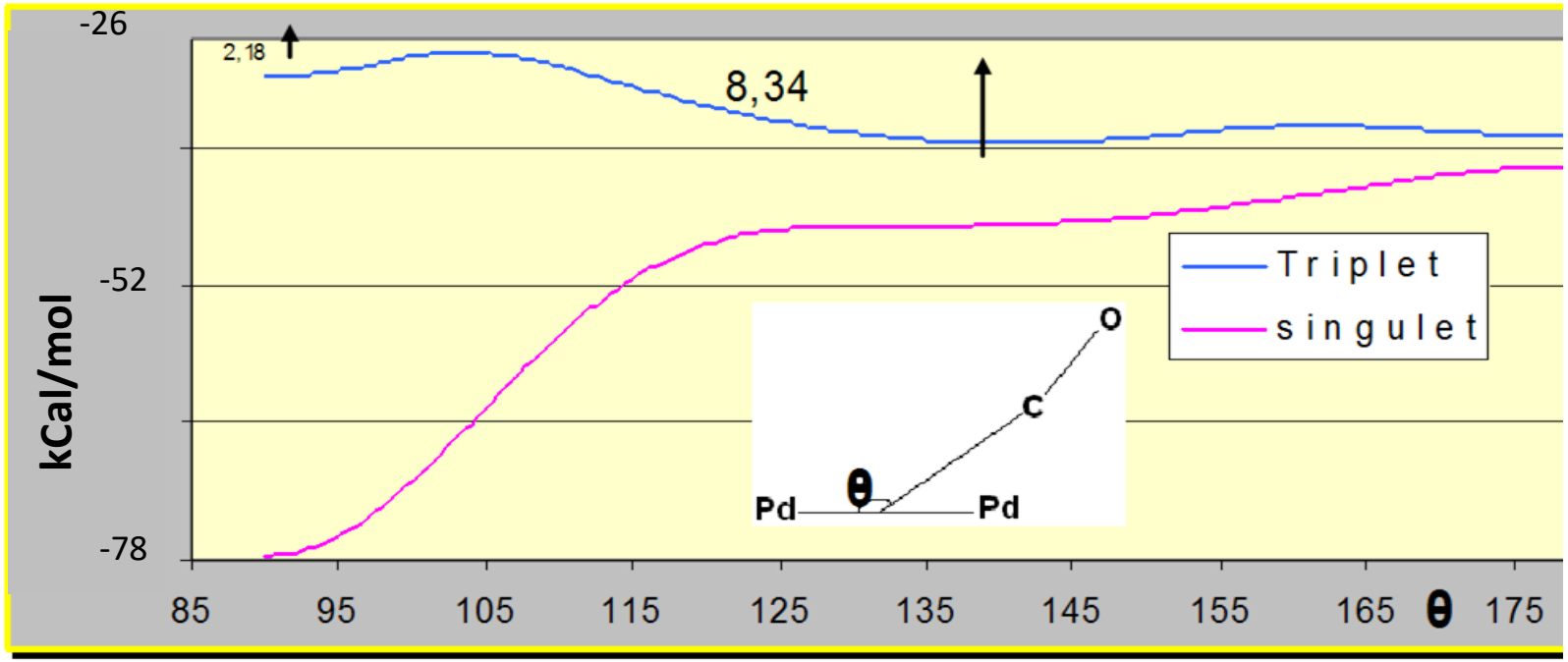
2015 cm^{-1}

2:1 with bridged structure

1856 cm^{-1}

From the calculations

- DFT with TPSS functional



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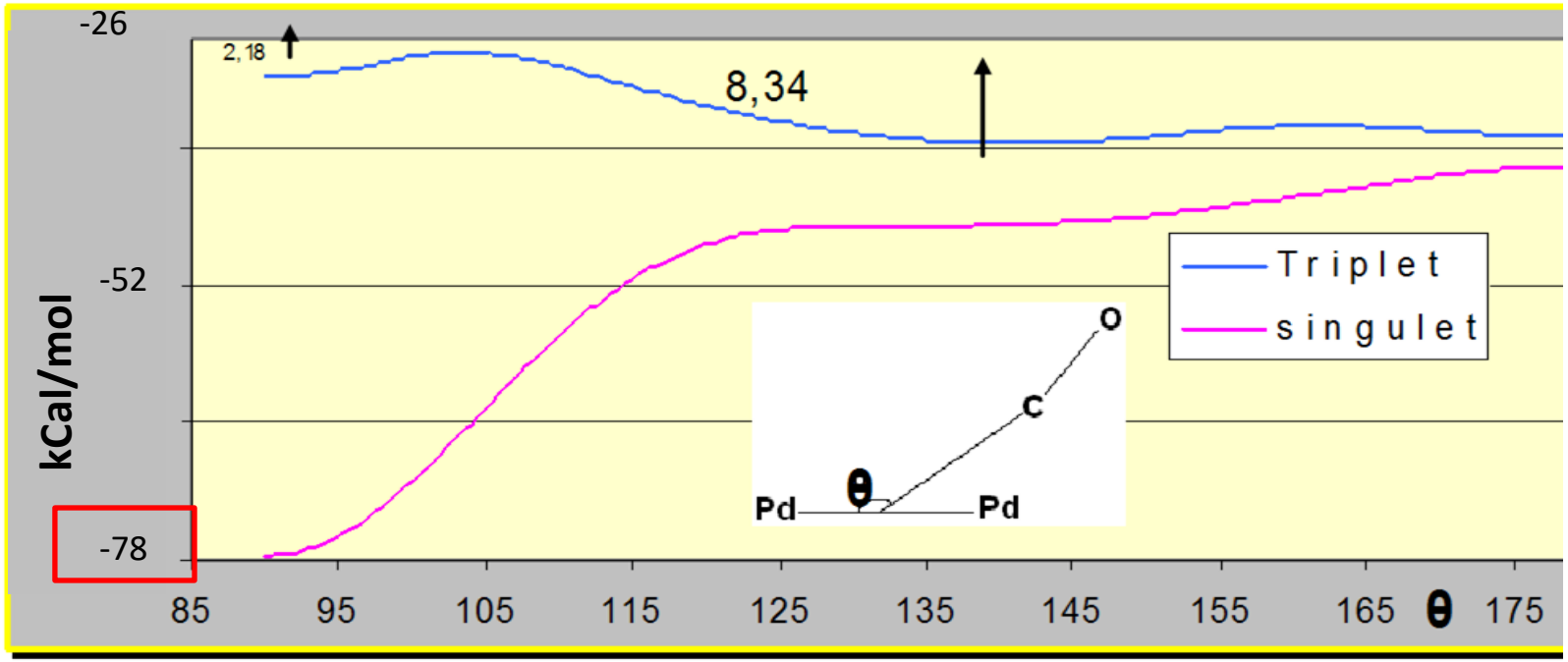
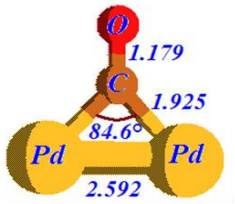
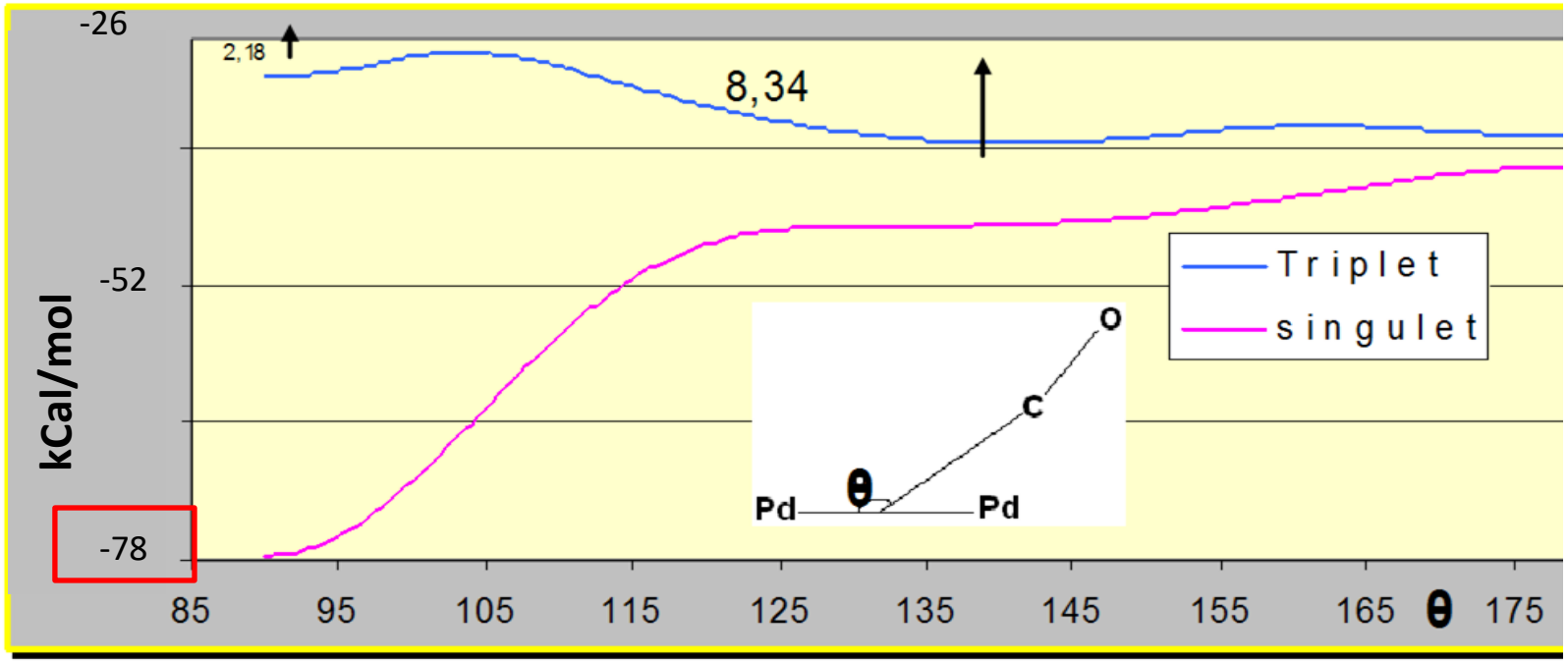
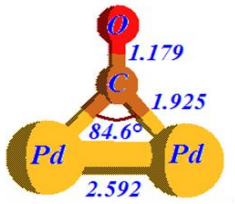




2:1 with bridged structure is the most stable isomer in the singulet state

From the calculations





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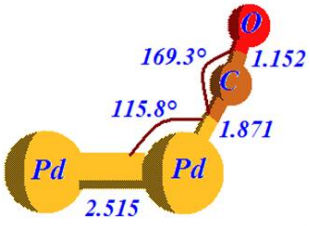
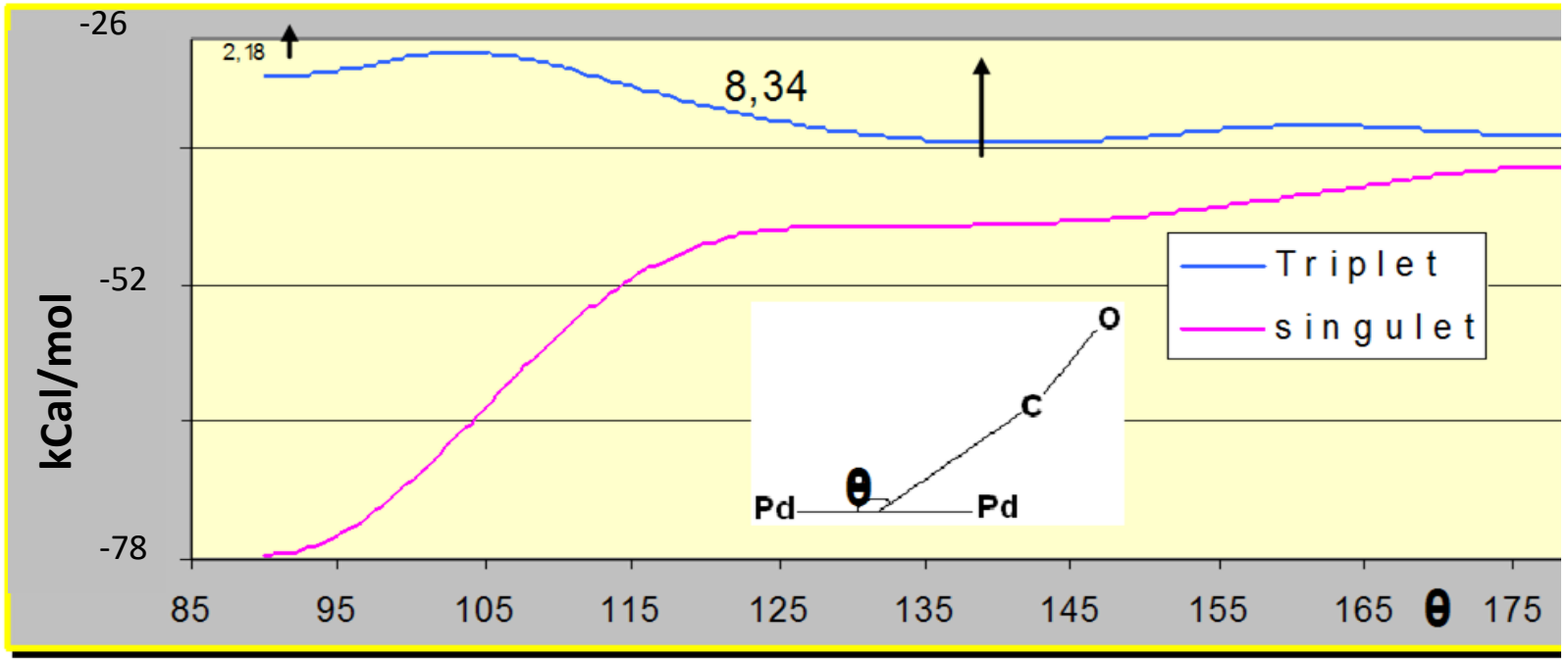
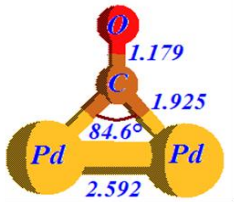
Argon and neon

From the calculations



2:1 with end-on structure in the triplet state : observed only in solid argon





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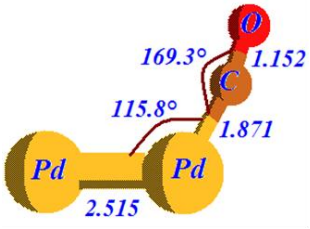


2:1 with end-on structure in the triplet state :

observed only in solid argon

	^{20}Ne	^{40}Ar	^{84}Kr	^{131}Xe	$^{14}N_2$
Polarizability (10^{-24} cm^3)	0.40	0.64	2.48	4.01	1.71

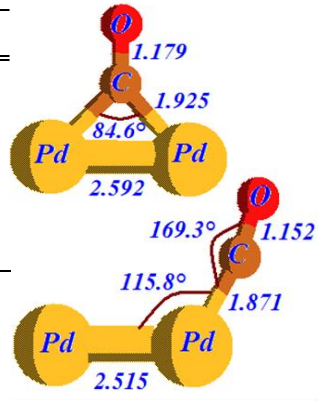
The higher polarizability of argon atoms stabilize this isomer

Comparison with the calculations

- DFT harmonic vibrational frequencies calculated with TPSS functional

Comparison with the calculations

	Mode	Experiment			DFT-TPSS		
		$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$	$^{12}C^{16}O$	$^{13}C^{16}O$	$^{12}C^{18}O$
2:1	γ_{PdCO}	387	-13	-4	369	-9	-2
br	δ_{OCPd}	588	-20	-2	575	-23	-3
	ν_{CO}	1857	-43	-41	1850	-41	-40
2:1	ν_{PdC}	484	-6	-14	454	-9	-14
eo	ν_{CO}	2015	-47	-44	2020	-46	-45



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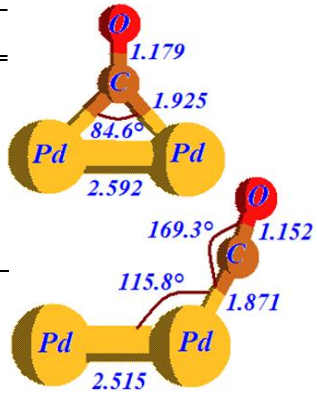
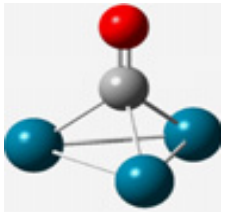
3:1	δ_{OCPd}	500	-17	-2	490	-17	-2
	ν_{CO}	1729	-39	-40	1730	-39	-40





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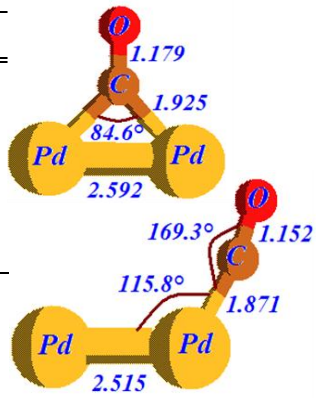
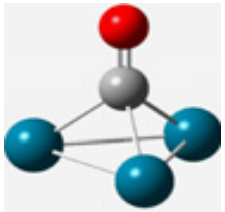
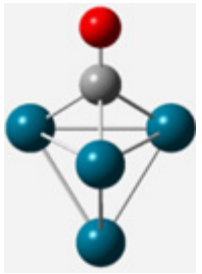
4:1	δ_{OCPd}	515	-17	-2	521	-19	-1
	ν_{CO}	1694	-39	-40	1687	-38	-40







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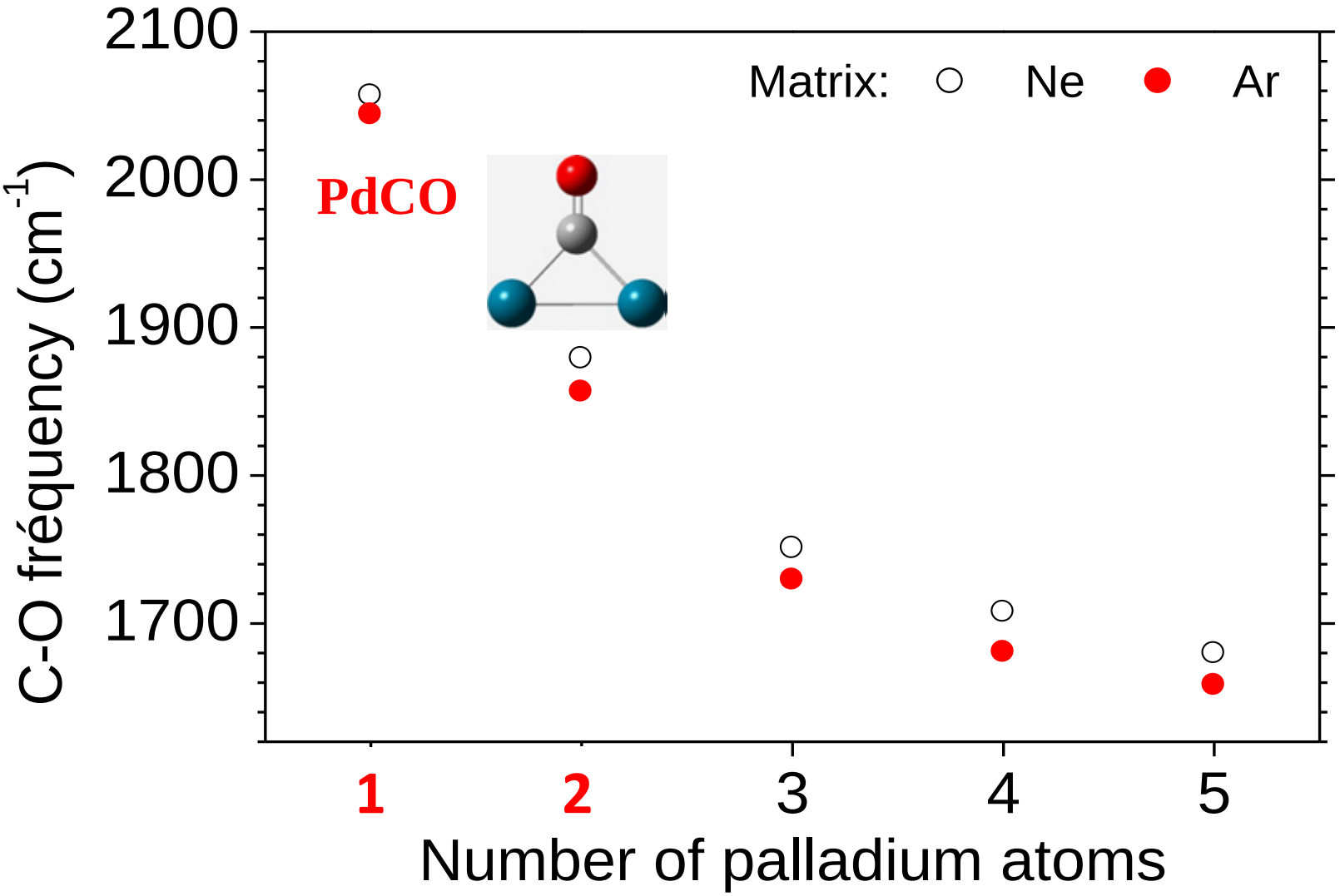
- The number of infrared active bands, their intensities, and their frequency positions provide insight into the structure and bonding of these complexes.

C-O frequency as a function of number of Pd atoms



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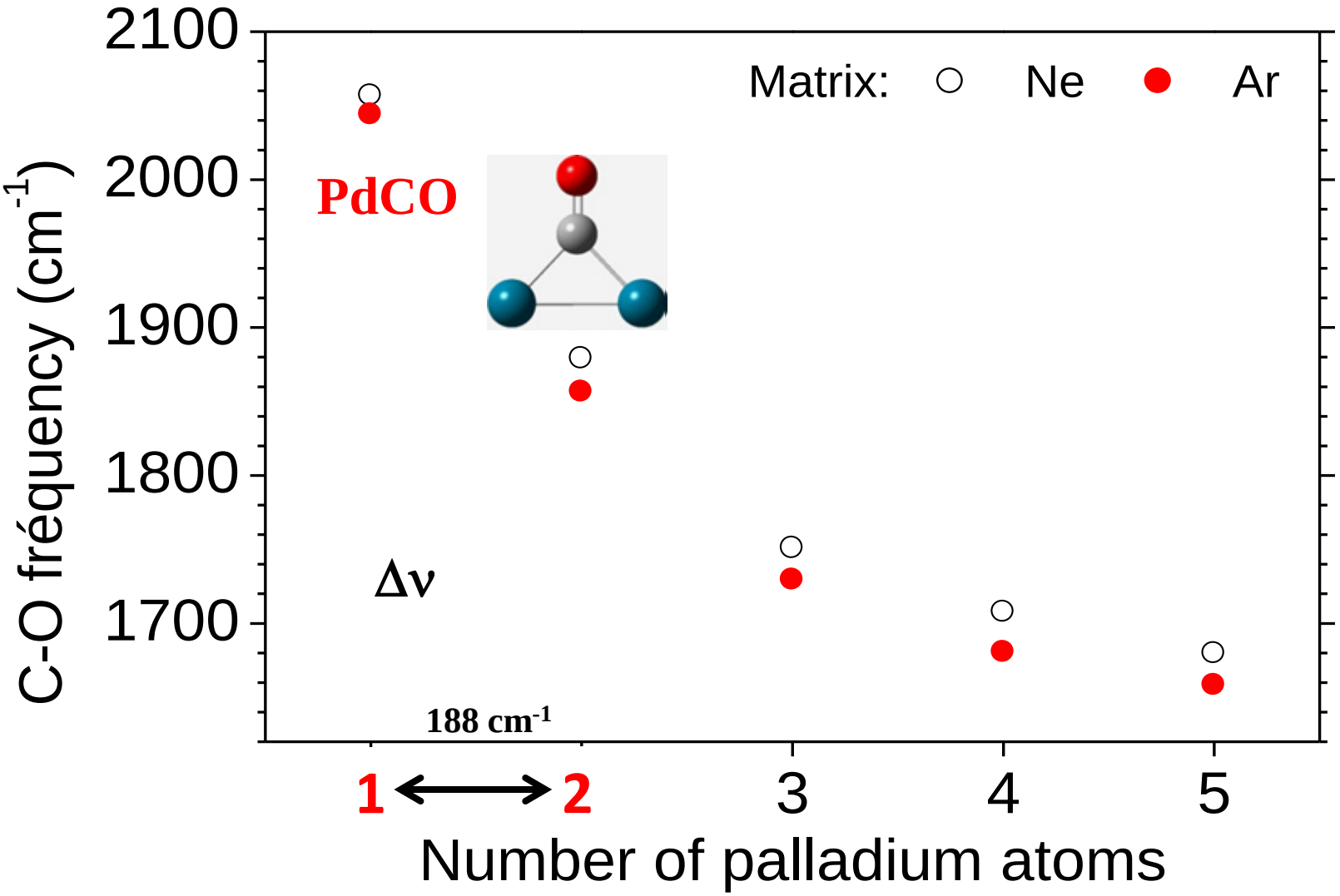

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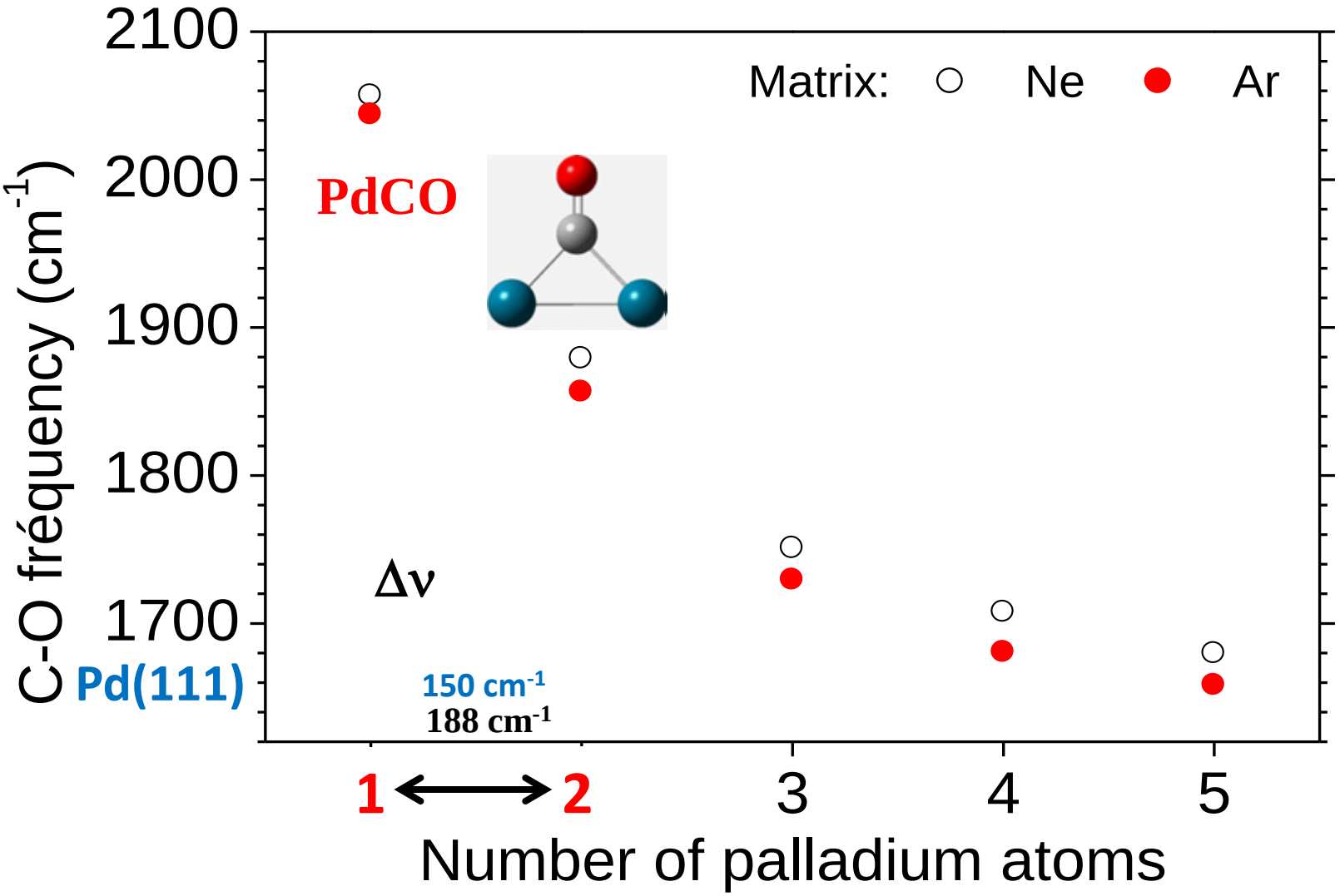

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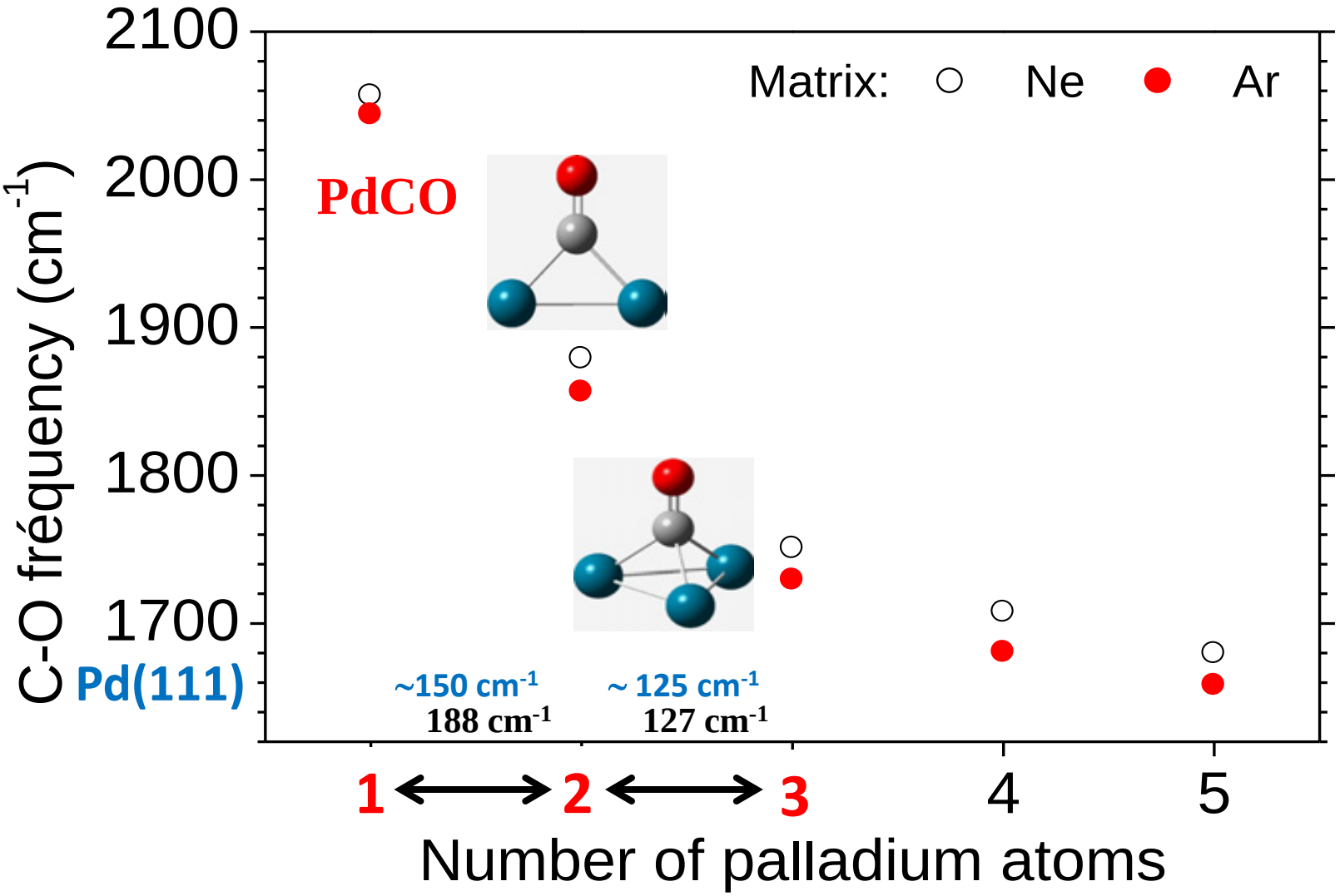

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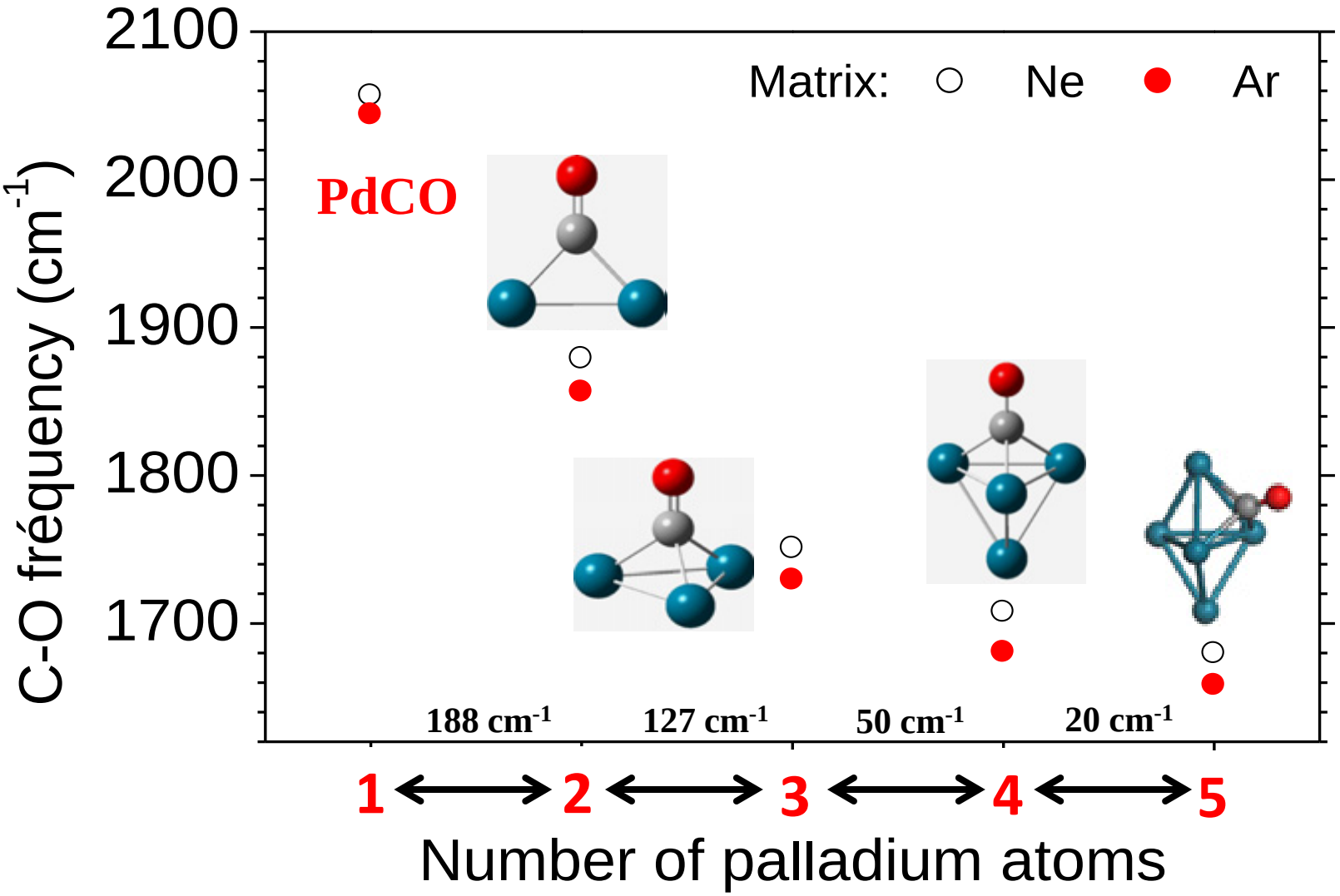

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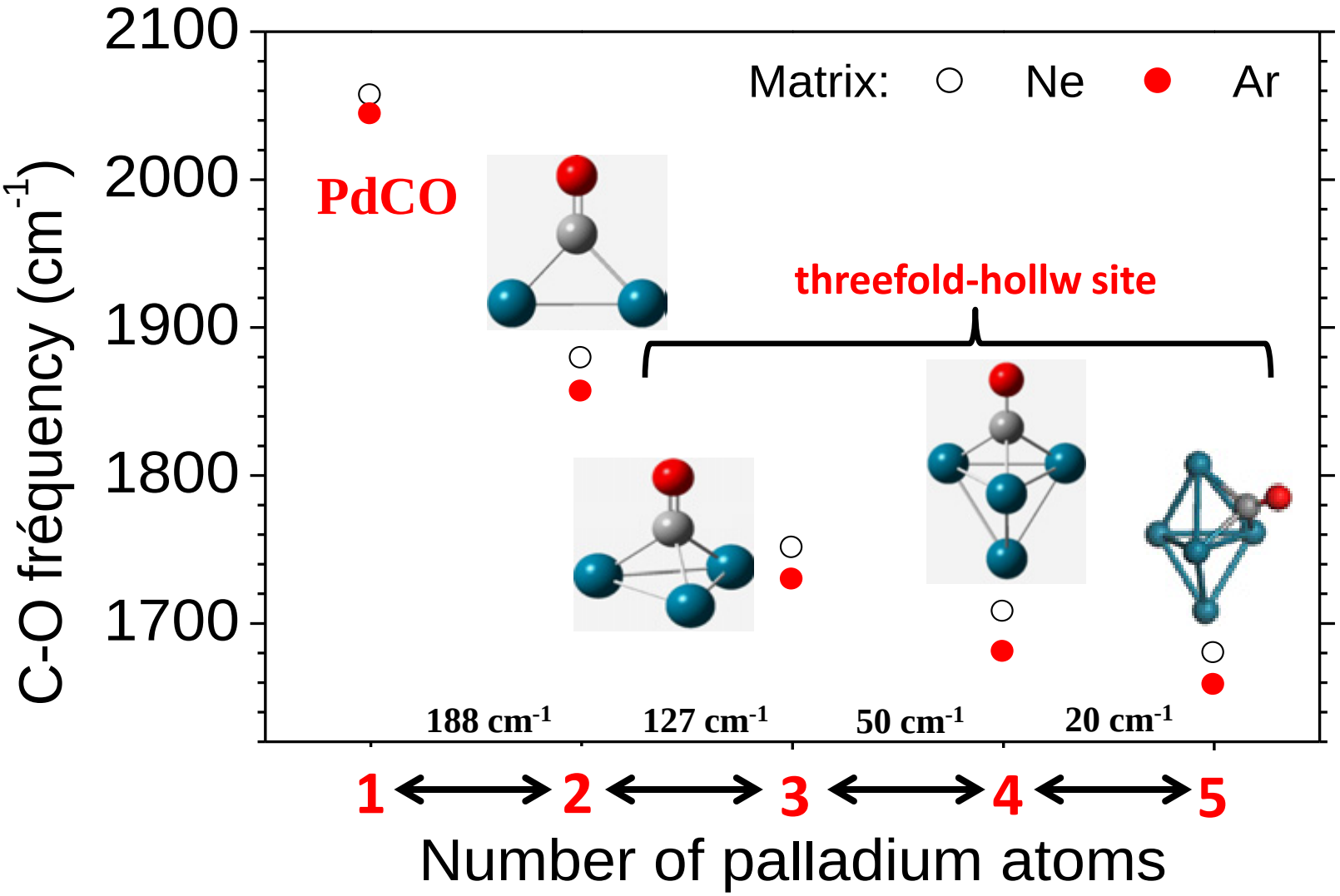

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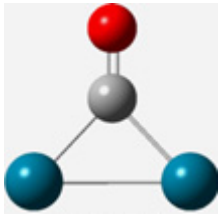
- These two isomers can be interconnected by photochemistry
- The theoretical analysis of the data perfectly support the experimental results.

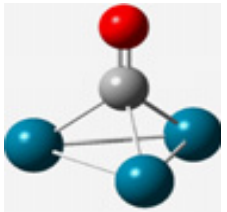
Thank you for your attention

$PdCO\ (^{1}\Sigma^{+}) + Pd\ (^{1}S) \rightarrow Pd_2CO\ (^{1}A_1)$ C_{2V}



$Pd_2\ (X\,^{3}\Sigma_u^{+}) + CO\ (^{1}\Sigma^{+}) \rightarrow Pd_2CO\ (^{3}A')$

$Pd_2CO\ (^{1}A_1) + Pd\ (^{1}S) \rightarrow Pd_3CO$ singulet C_{3V}



$Pd_3CO + Pd\ (^{1}S) \rightarrow Pd_4CO$ singulet C_{3V}